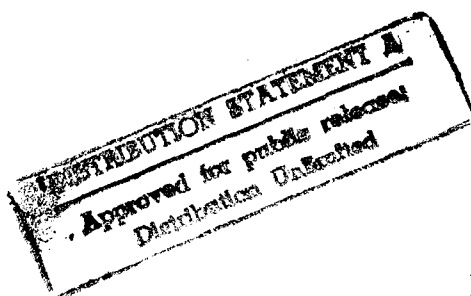


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# STRATEGIC INVESTMENT PLAN FISCAL YEAR 1993



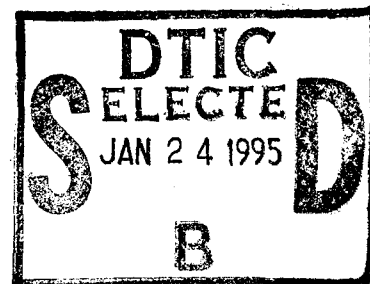
## STRATEGIC ENVIRONMENTAL RESEARCH AND DEVELOPMENT PROGRAM



September 1993  
(FINAL)

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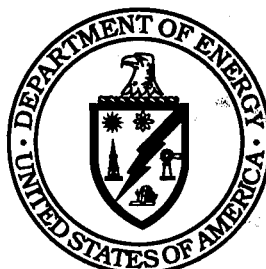


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# STRATEGIC INVESTMENT PLAN FISCAL YEAR 1993



## STRATEGIC ENVIRONMENTAL RESEARCH AND DEVELOPMENT PROGRAM

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(FINAL)

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## FOREWORD

The Strategic Environmental Research And Development Program (SERDP) is mandated in 10 U.S.C. §§2091-2904. SERDP addresses environmental matters of concern to the Department of Defense (DoD) and the Department of Energy (DOE). It is conducted as a tri-agency program with participation from the DoD, DOE and Environmental Protection Agency (EPA).

This report includes information required by title 10 U.S.C. § 2902 for the annual report to Congress. It includes project descriptions and allocated funding and is divided into six technology thrust areas; 1) Alternate/Clean Energy, 2) Compliance, 3) Conservation, 4) Global Environmental Change, 5) Installation Restoration, and 6) Pollution Prevention. The individual research projects were reviewed and selected by the SERDP Council in response to specific requirements for research and development. All programs greater than or equal to \$1,000,000 were recommended after review by the SERDP Scientific Advisory Board. The FY 1993 SERDP Strategic Investment Plan is based on a funding target of \$180 million. The approved projects are submitted on behalf of the SERDP Council whose membership consists of: the Assistant Secretary of Defense, Production and Logistics; the Director of Defense Research and Engineering; the Vice Chairman of the Joint Chiefs of Staff and representatives from each of the Services and Coast Guard; the Assistant Secretary of the Air Force, Space; the Assistant Secretary of Energy for Defense Programs; the Assistant Secretary of Energy for Environmental Restoration and Waste Management; the Director of the DOE Office of Energy Research; and the Administrator of the EPA.

## ACRONYMS

A	Army
AF	Air Force
ARPA	Advanced Research Projects Agency
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CWA	Clean Water Act
DDR&E	Director, Defense Research and Engineering
DOE	Department of Energy
DoD	Department of Defense
DNA	Defense Nuclear Agency
DSPO	Defense Support Projects Office
EPA	Environmental Protection Agency
IR	Installation Restoration
N	Navy
R&D	Research and Development
RCRA	Resource Conservation and Recovery Act
SARA	Superfund Amendments and Reauthorization Act
SERDP	Strategic Environmental Research and Development Program
SITE	Superfund Innovative Technology Evaluation
TTAWG	Technology Thrust Area Working Group
USGCRP	U.S. Global Change Research Program

## **EXECUTIVE SUMMARY**

### **Overview**

FY 1993 Strategic Environmental Research and Development Program (SERDP) efforts continue to emphasize assessing the state of global atmospheric and ocean environments; the effectiveness of remediation technologies to address the Departments of Defense (DoD) and Energy (DOE) environmental obligations; approaches to minimize, treat, and dispose of hazardous waste; methods for assessing hazards in existing and restored sites; and alternative and clean energy options for use by DoD facilities and operations.

Several new initiatives have commenced that will enhance our ability to successfully address the above targeted areas. SERDP has identified six technology thrust areas versus the three areas found in past programs. These are: Global Environmental Change (formerly Remote Sensing), Alternate/Clean Energy, Installation Restoration, Pollution Prevention, Compliance, and Conservation. The last four technology thrusts map directly with the pillars found within the Tri-Service Environmental Quality Strategic Research and Development Plan (EQ Strat Plan) as developed under the Services' Reliance technology coordinating mechanism. Thus, SERDP can now take advantage of existing technology coordinating bodies to further identify and define R&D opportunities for investment in response to known requirements for R&D as developed by the Reliance mechanism, and then provide sufficient resources to reach "critical mass" in order to address specific, difficult environmental challenges.

### **Global Environmental Change**

Global Environmental Change research includes acquisition/organization of data and research results that quantitatively describe the total environment at global and regional scales. Integration of the new and existing programs in data collection and analysis methodologies, process study research and environmental modeling are keystones of this effort capitalizing on agency unique capabilities that fully leverage the U.S. Global Change Research Program (USGCRP).

Representative activities include: improving access to existing DoD and DOE data bases and facilities; developing, demonstrating, and applying DoD, DOE, and EPA remote sensing capabilities and technologies to support environmental change research and establish enhanced observation strategies and systems; and enhance environmental process research and modeling.

A significant portion of the FY 1993 SERDP program (35 percent) is devoted to the execution of Phase I programs that were delayed due to rescission action in FY 1992. FY 1993 funds will enhance funds provided by the FY 1992 Supplemental Appropriation to satisfy the initial requests of the approved Phase I efforts.

## **Alternate/Clean Energy**

This area includes research on environmentally sound alternative energy sources to reduce dependence on petroleum-based sources, overall energy consumption, energy costs and "greenhouse effects."

Representative activities include: research and demonstration on expanded use of renewable energy resources, such as geothermal, solar photovoltaic, wind and hydropower; research and technology demonstration on innovative, substitute, alternative energy sources to reduce emissions and fossil fuel consumption; and research and demonstration on reduced energy consuming techniques, components and power units/sources that contribute to reduced energy consumption.

## **Installation Restoration**

This area focuses on technology development and demonstration for more efficient, effective environmental cleanup of soil, sediment, groundwater, surface water and structures contaminated with hazardous, radioactive and toxic materials from past activities. Cleanup/remediation techniques, treatment technologies and monitoring assessment methods are the principle focus of this area.

Other representative activities include: developing and demonstrating (not whole site cleanup) innovative technologies or techniques for handling hazardous waste or materials of particular concern or uniqueness to defense programs; developing and demonstrating innovative site characterization techniques; developing and demonstrating innovative monitoring techniques (chemical and biological) to gather data before restoration begins, during the operations, and after it is completed; and developing and demonstrating innovative technologies for assessing fate and transport effects.

## **Pollution Prevention**

Pollution Prevention means "source reduction," as defined under the Pollution Prevention Act of 1990 and other practices that reduce or eliminate the creation of pollutants through increased efficiency in the use of raw materials including energy, water and other resources, or materials substitution. The term includes: equipment or technology modifications, process or procedure modifications, reformulation or redesign of products, substitution of materials and improvements in housekeeping, maintenance, training, or inventory control. Under the Pollution Prevention Act, end-of-pipe recycling, energy recovery, treatment, and disposal are not included within the definition of pollution prevention. Practices commonly described as "in-process recycling" qualify as pollution prevention.

Representative activities include: developing and/or evaluating innovative pollution prevention technologies, processes and environmental management techniques for reducing or

eliminating wastes, effluents, or emissions at DoD/DOE processes and facilities; research on protective coating/coating removal, and process modification, substitute processing chemicals and alternative processes to reduce or eliminate hazardous waste generated by electroplating, paint stripping and metal cleaning operations; process modeling to eliminate or minimize the waste stream; and research to identify alternatives to introducing hazardous materials into an in-process waste stream in order to render that waste stream environmentally acceptable, preferably benign.

## **Compliance**

This area includes technologies for environmental monitoring, waste treatment, end-of-pipe recycling and disposal, and environmental management not directly related to site restoration, but related to meeting current and future environmental compliance requirements. It includes understanding the fate and transport of defense related wastes and pollutants as well as methods and techniques for mitigating ecological and health impacts of these materials in the environment.

Representative Activities include: developing monitoring and assessment tools related to environmental compliance and management; developing source treatment and control technologies for installation support operations (waste, waste water, solid waste management and air pollution); developing new treatment and control technologies for hazardous wastes resulting from energetics production, manufacturing, and maintenance operations; research to ascertain the toxicological effect to humans and ecosystems from exposure to chemicals and materials used in defense activities; and research on environmentally and economically acceptable alternatives to open burning or open detonation of liquid rocket propellants, munitions and energetic materials.

## **Conservation**

This area is focused on research toward understanding, protecting, and maintaining biophysical resources and facilities relative to material and cultural resources in order to ensure: (1) compliance with environmental laws; (2) sustained use of land and coastal resources; and (3) support for stewardship of those resources on relevant federal lands. Those resources include all biophysical resources associated with and related to ecosystems and habitat, e.g. soils, vegetation, landform, water and biodiversity; and facilities and landform associated with historic and archeological resources. Efforts are intended to: (1) effectively predict the presence, quantity and quality of natural and cultural resources; (2) improve the knowledge of the basic processes of these resources as they relate to, and are impacted by, use of lands; and (3) advance the technology to mitigate, rehabilitate, and maintain these resources.

Representative activities include: developing and advancing remote, field data collection techniques to locate and quantify resources; developing an understanding of species-species and species-habitat relationships and how they are affected by federal land

use; developing long-term, multiple use management strategies to optimize resource protection; and developing proactive land use and management tools and techniques to protect threatened and endanger resources and habitats.

## **Initiatives**

In FY 1993 under SERDP the Department is continuing to build a closer coupling of DoD, DOE and EPA research efforts. The intent is to focus on DoD/DOE needs by means of the SERDP management structure specified in the implementing legislation. Key SERDP initiatives for FY 1993 that build upon the joint approach include:

- National DoD Installation Restoration Technology Demonstration Sites
- Joint DoD/DOE Program for Clean, Agile Manufacturing Technology for Propellants, Explosives and Pyrotechnics
- Pilot projects associated with the activities of the Gore-Gates Environmental Task Force

### **1. National DoD Installation Restoration Technology Demonstration Sites**

The recent emphasis placed on expediting remediation efforts of DoD/DOE facilities has likewise encouraged the development of novel remediation technologies. Unfortunately, their accomplishments have not been efficiently, nor effectively, transitioned to other technologists and the users within other federal agencies and the private sector. Inconsistencies in the conduct of site characterization, data collection and assessment, and incomplete dissemination of the attributes and value of the demonstration have all contributed to this inefficient process.

One of the major initiatives commencing this year is the establishment of six national DoD environmental technology demonstration sites. These sites will provide the ability to conduct side-by-side demonstrations of technologies developed either in the federal or private sector. The National DoD Environmental Technology Demonstration Program (NETDP) proposal offers an alternative to help reduce the duplication of effort and inefficiencies associated with the current system and promote rapid transfer of technology to field applications.

The NETDP uses the Reliance agreements as its foundation. It focuses on the demonstration of remediation technologies that respond to the primary needs of the Services. As the principal manufacturer of field weapons, the Army has been given the lead in the area of energetics materials remediation technology, and the Navy and Air Force have been given primary responsibility for technology development in the area of petroleum, oils, lubricants (POL) and solvents. Each development task is conducted within this Reliance framework which is subordinate to the Environmental Quality Technology Panel under the Joint



Engineers coordinating committee.

While Reliance has provided a coordinating mechanism for the conduct of remediation technology development, it has not yet provided the support necessary to bring together technologies for side-by-side comparison, standardization of data collection and analysis, and publication of user guides and engineering design specifications. The Tri-Service NETDP proposal has this objective in mind and SERDP funds are proposed to achieve this objective.

## **2. Joint DoD/DOE Program for Clean, Agile Manufacturing Technology for Propellants, Explosives and Pyrotechnics**

The Department of Defense is required to reduce the hazardous wastes associated with production of weapons systems using propellants, explosives, and pyrotechnics (PEP) by at least 50 percent by 1997. The Department of Energy and the National Aeronautics and Space Administration (NASA) also have PEP waste reduction requirements. Approximately 500 million pounds of PEP are produced each year for DoD, DOE, and NASA as main charge explosives, solid rocket propellants, and flares/illuminators. PEP chemicals and products are produced in government operated, government owned-contractor operated (GOCO), and defense contractor facilities. Future waste reduction can be achieved by reducing wastes throughout the PEP product life cycle. The product life cycle includes synthesis of PEP chemicals; formulation of chemicals into a product; chemical processing, loading, and unloading of the product; combustion emissions; and methods to reclaim, recover, and recycle excess material.

The goal of this initiative is to develop integrated product/process development (IPPD) technologies and tools to achieve a design for reconfiguring existing PEP production facilities into agile factories which will reduce total life cycle wastes by over 90 percent from the 1992 PEP waste baseline.

The technical approach is for governmental and industrial PEP R&D labs, pilot plants, and production facilities to be organized into a program network. Present products, processes, PEP chemicals, and technologies will be surveyed. Models and simulations will predict life cycle performance. Pollution prevention technologies and new factory concepts will be experimentally tested in existing facilities. When use of existing facilities is not practical, a special demonstration testbed may be built. The factory design will then be developed, including detailed descriptions of products, chemical engineering unit operations, utility requirements, regulatory and qualification approaches, safety, and pollution prevention devices to be used in its operation.

## **3. Gore-Gates Environmental Task Force (ETF)**

The ETF was formed in response to a Congressional request to create a team of scientists with appropriate security clearances to work with the government and determine the applicability of classified systems and data to environmental science.

The scientists comprising the ETF are reviewing:

- the environmental community's information needs
- past, present, and near-term classified systems and data/archives
- current government efforts that apply classified data to environmental issues.

The ETF scientists will recommend release of specific classified information of value to the environmental community as well as follow-on research opportunities. An environmental security policy group has been activated with Service and Defense Agency participation. The Department is working with the Intelligence community to develop procedures for environmental requirements to compete on a routine basis for tasking of intelligence systems.

### **Congressional Interest Items**

The SERDP FY 1993 Strategic Investment Plan includes five projects of interest to the Congress as separate projects within various technology thrust areas.

In the FY 1993 Department of Defense Appropriations Conference Report, H.R. Report 102-1015, Congress allocated \$3,500,000 to support bioremediation research efforts. A project entitled "Applied Demonstration Program in Environmental Compliance and Bioremediation Technology" has been funded under the Installation Restoration Thrust Area. The Report also identifies \$5,000,000 in support for the work performed on data access by the Consortium for International Earth Science Information Network (CIESIN). "Strategic Environmental Distributed Active Archive Resources", a project within the Global Environmental Change Thrust Area, outlines the proposed work of the Consortium. Finally, the Report provides \$500,000 for the efforts of the Coalition for International Environmental Research and Assistance (CIERA). Their project found within the Conservation Thrust Area and entitled, "Information Support for Environmental Management", is focused on the development of an environmental manager's decision support system for the management of habitats on DoD and other government owned lands, and conducted in conjunction with the Army's Topographic Engineering Center.

The Department of Defense Appropriations Bill, Senate Appropriations Committee, S.R. Report 102-408, requests that a study be conducted on the potential for the abyssal plains of the oceans for use as a repository of hazardous wastes. The U.S. Naval Research Laboratory has proposed an effort, entitled "Abyssal Plains Study", which will comply with direction as provided in the Report. The proposal may be found within the Compliance Thrust Area.

The Supplemental Appropriations Transfer and Rescission Bill of FY 1992, S.R. Report 102-395, provided support for electron scrubbing technology development. This year, SERDP will provide follow-on funds to complete the technology demonstration. "e-SCRUB - The Application of DNA Pulsed Power to Electron Scrubbing of Flue Gas to Remove Unwanted By-products" is found within the Compliance Thrust Area.

# **Funding Summary \$(000)**

Global Environmental Change	\$ 65,200
Alternate/Clean Energy	\$ 8,100
Installation Restoration	\$ 30,047
Pollution Prevention	\$ 31,782
Compliance	\$ 12,637
Conservation	\$ 8,164
Congressional Interest Items	\$ 11,583
Other	<u>\$ 12,487</u>
<b>TOTAL</b>	<b>\$180,000</b>

## Alternate/Clean Energy

Project Title	Page Number	Funding FY93 (K)
<b>Applications of Alternate/Clean Energy Sources to DoD Facilities</b>		
Photovoltaics for Military Applications (DOE)	9	4,000
Fuel Cells for Military Applications (A)	15	350
Low Energy Model Installation Program (A)	19	1,400
Geothermal Heat Pumps/Enhanced Building Envelopes (DOE)	22	600
Advanced Cycle Mobile Heat Pump (AF)	25	500
Utilization of Biomass Technologies on Military Installations (EPA)	27	750
<b>Technology Demonstrations of Alternate/Clean Energy Sources</b>		
Pilot Plant Demonstration of Methanol Using the HYDROCARB Process with Biomass Feedstock (EPA)	31	500
Total		8,100

## **SERDP Thrust Area: Alternate/Clean Energy**

### **Title: Photovoltaics for Military Applications**

#### **Problem Statement:**

The goal of this project is to do technology demonstration/technology transfer of PV technology in Intermediate/Large Remote and Grid Interactive applications thereby promoting implementation in other Department of Defense (DoD) applications. This will reduce the amount of pollutants from fossil-fueled electrical gensets within the DoD and enhance energy security.

DoD is the largest single user of energy in the world with an annual energy consumption of 150 million barrels of oil equivalent at a yearly cost of over \$3 Billion. Since DoD relies on conventional sources of power and energy (coal, fuel oil, diesel, natural gas, etc.), DoD is a significant contributor to environmental pollution from energy production and use. Photovoltaic power systems have been successfully demonstrated in small/intermediate sizes (up to 60 KW), both stand-alone and hybrid (PV/Diesel). The technology is commercialized and industry has an operational manufacturing capability. Photovoltaic power systems can be of significant help in reducing energy and O&M costs and eliminating air pollutants in areas where DoD generates its own power and increasing energy security.

#### **Project Description:**

The technical objective is to demonstrate the use of PV technology (inverters, power processing controls) in systems for Intermediate/Large Remote and Grid Interactive applications that meet DoD requirements.

The most promising application for renewable power sources in the next 30 years is to augment conventional power sources to optimize the efficiency of both the conventional and renewable sources to reduce cost and environmental impacts. Example applications range from stand-alone renewable/engine power sources to demand reduction on the grid. The common denominator of these applications is the need for battery energy storage to decouple power generation from power demand and a power processing center (PPC) to integrate the generation sources in a way that optimizes the utilization of each source. The only obstacle to these applications is that the PPC is not an off-the-shelf product and must be custom designed and manufactured for each application.

#### **Technical Approach/Tasks:**

The focus of this Phase III SERDP effort is to develop a modular, standardized PPC that will service multiple source PV/engine hybrid and demand reduction applications. The basic PPC will be in the 50 kW size range that can be paralleled for applications up to 500 kW. This size range represents the bulk of hybrid and grid-support applications not only in the DoD, but in other government agencies like the National Parks Service, Fish and Wildlife, the National Forest Service, and the Bureau of Land Management. This effort will leverage SERDP monies for the benefit of many government agencies.

The Phase I effort focuses on smaller PV/engine hybrid applications and grid-support to extend service life of transmission and distribution systems. The Phase III effort expands on the prior effort to larger systems and to include small demand reduction applications. The structure of the Phase III effort will be similar to prior efforts and will include three tasks: 1. Application Evaluation, 2. Hardware Development, and 3. Applications Validation. The funding breakdown is modified to emphasize hardware development and to field one larger system of a size range of 200-300 kW PPC. Also, as was the case in Phase I, SERDP monies will provide technical support for ECIP projects.

The technical approach will also be similar to Phase I. It will build on prior results and lessons learned. The first task is to identify, evaluate and select Phase III projects. Phase I establishes a computerized data base to organize and process information on DoD facilities and their power needs. By the time Phase III is initiated, candidate facilities will be identified by examining the existing data base. The candidate sites will be visited and evaluated, and the Phase III projects will be selected.

Application evaluation funds will also be used for administrative support throughout the project and to determine the life-cycle environmental cost savings associated with alternative/clean energy. The environmental studies will be performed with guidance from the Environmental Protection Agency (EPA). The EPA Air and Energy Research Laboratory has agreed to participate in and monitor the development of a life-cycle environmental methodology and to apply the methodology to determine the cost savings.

The facility will develop an RFP for a turn-key system under guidance from the PV Review Committee and Sandia. The system RFP will include specifications for a modular and flexible PPC. A stipulation of the RFP is that the PPC must submit to acceptance testing at an independent facility defined and selected by the DoD PV Review Committee and Sandia. After installation, Sandia will perform an initial system evaluation for system acceptance and to establish the baseline performance, and another evaluation after one year of operation to validate the technology.

This program will be directly responsive to the 1990 House Defense Authorization Act that requires the installation of 100 MW of renewable energy by 1996. Additionally, Presidential Executive Order 12579 requires DoD, along with other Federal Agencies, to reduce energy consumption by 20% and to offset energy production using renewable energy where life cycle cost effective. The recently enacted Energy Policy Act of 1992, contains several provisions consistent with the expansion of the use of PV in all sectors, including the DoD.

The table below details the funding from other sources. It is important to stress that SERDP fills a programmatic need for the DoD PV program. The primary expected source of funds (other than SERDP) is the Energy Conservation Investment Program (ECIP) which is part of the Military Construction Program (MCP). Funds appropriated as part of the MCP must be used for hardware, not supplemental related activities such as resource assessment, application identification, and project selection activities.

**Table 1 - Total Funding for DoD PV Program**

	<b>Non-SERDP Funding - \$ Millions</b>				
<b>Fiscal Year</b>	<b>1991</b>	<b>1992</b>	<b>1993</b>	<b>1994</b>	<b>Total</b>
Project Development	0.4	1.0	0.5	0.5	2.4
Project Implementation	---	6.0	10.0	5.0	21.0
Monitor and Analyze	---	0.3	0.3	0.3	0.9
Technology Transfer	---	0.1	0.1	0.1	0.3
<b>TOTAL Non-SERDP</b>	<b>0.4</b>	<b>7.4</b>	<b>10.9</b>	<b>5.9</b>	<b>24.6</b>
SERDP	* 4.0	---	4.0	4.0	12.0
<b>TOTAL</b>	<b>4.4</b>	<b>7.4</b>	<b>14.9</b>	<b>9.9</b>	<b>36.6</b>
*Not Received until 8 December 1992					

**Expected Payoff:**

Over the long-term, a significant reduction in the amount of pollutants from fossil fuel-burning generators now used in the DoD. According to some estimates, the Department of Defense annual emissions are:

720 million tons of CO<sub>2</sub>  
 1.15 million tons of NO<sub>x</sub>  
 740,000 Tons of SO<sub>x</sub>

Of this amount, we estimate that a significant portion of the emissions are from fossil fuel (primarily Diesel) gensets as shown below. Significantly, the physical location and accessibility of existing diesel generators is such that the total cost of running a diesel is many times the amount usually attributed only to the cost of fuel. The result is that PV projects are often times economically competitive using the Department of Defense's measures of merit---the simple payback period and the savings-to-investment ratio. The estimated annual savings potential is shown in the last column.

**Table 2 - Pollution Estimate from Diesel Generators in DoD**

Application Class	Tons of Pollutants			Annual Savings Potential - \$M
	CO <sub>2</sub>	NO <sub>x</sub>	SO <sub>x</sub>	
Small	31,700	723	32	95
Intermediate-Large	127,000	2,900	128	200
Grid-Interactive	285,000	6,500	290	200+
Total	443,700	10,123	450	495+

Note: The analysis for the above table was developed for the July 28, 1992 briefing to the SERDP Scientific Advisory Board. The analysis was based on data from the DoD Defense Energy Installation Survey, an in-house Army Construction Engineering Research Laboratory (CERL) methodology for estimating emissions, and the Total Emission Model for Integrated Systems (TEMIS), and unpublished China Lake Navy Energy Office work.

#### **Transition Plan:**

To illustrate the process to be followed for the introduction and utilization of photovoltaics in the DoD, consider one of the projects selected for a hybrid (PV-diesel genset) at an electronic warfare simulator facility on San Clemente Island (a Navy owned island about 70 miles off the coast of San Diego). The sequence of events is as follows:

1988-1991 - Discussions by Navy member of the PV Review Committee about feasibility, nature of load profile, insolation, etc.

Early 1992 - Decision by the user, the Naval Command and Control Ocean Surveillance Center (NCCOSC) to contract for an applications assessment. Funds were provided by the Navy Energy Office, China Lake. It should be noted that the absence of a source of funds (such as SERDP) to do an applications assessment delayed the project at least 2 years.

April-August 1992 - Applications assessment, including a conceptual design illustrating that a system could be built that is technically feasible and competitive from a savings-to-investment ratio and simple payback period --- the figures of merit that are used in the Energy Conservation Investment Program (ECIP).

October 1992 to Present - NCCOSC has agreed to initiate a competitive RFP, has named a program manager, has initiated the justification paperwork through channels, has formed a technical advisory team that includes the Sandia National Laboratories representative. The prospect of SERDP funding allowed Sandia to make the appropriate technical personnel available.



Industry ability to assume production: The PV industry is capable of providing mature PV modules and battery technology, the two highest cost components of a PV system. Power conditioning and control systems for hybrid systems above 25 kW are not standard off-the-shelf items because there has not been enough need to sustain a market. Sandia National Laboratories Design Assistance Center is developing a program (in cooperation with the Navy Civil Engineering Laboratory) to cooperatively work with industry to develop that capability. The approach is for industry to supply a turn-key system to meet the requirements stated in the procurement documentation.

Coordination between performer and user: Inherent in the process already existing in the DoD PV Program is the requirement that there be a strong user involvement in the identification, categorization, selection, and procurement of a PV system. The user is required to take the initiative to get the project approved through the applicable chain of command, to provide the procurement capability to acquire the system, and to make the system available for data collection after it is installed.

#### **Milestones:**

February 1993 - Competitive RFP to be completed.

June 1993 - Release of competitive RFP.

Late 1993 - Selection of contractor for systems design and installation.

Mid 1994 - Installation and IOC for PV Hybrid system.

One year after installation - monitoring of system performance by the PV Review Committee and Sandia National Laboratories (funded by SERDP).

We anticipate that there will be 5-7 different PV-diesel hybrid projects initiated during calendar 1993. Some will be funded primarily from SERDP funds. As different military organizations develop their own approach to their systems, the PV Review Committee in cooperation with the DOE Sandia National Laboratories, will develop an in-service capability to investigate, contract for, install and maintain PV systems. Existing military in-service technical schools and logistics will reflect the wider use of photovoltaics. Each system will have its own unique features, but the involvement and eventual ownership of the systems will be a common feature of each. SERDP funding is absolutely vital to maintain continuity.

#### **Funding: (\$K)**

<b>Task</b>	<b>Funding</b>	<b>Start Date (FY)</b>	<b>Stop Date (FY)</b>
Application Evaluation	250 K	6/93	12/94
Hardware Development	1750 K	9/93	9/94
Application Validation	2000 K	12/93	12/94

**Outyear funding plan to reflect transition:**

We propose that SERDP funds be provided at a \$4.0 million level per year through FY 95.

**Performers:**

Department of Defense, Department of Energy, Sandia National Laboratories

Industry has significant involvement in this project. Industry will provide all hardware, system design and installation, resource assessment, and application assessments. Currently, there are no formal Cooperative Research and Development Agreements (CRADA) as specified in the National Competitiveness Technology Transfer Act of 1982 contemplated; however, the DoD and DOE consider this a cooperative joint agency program.

**Technical Points of Contact:**

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## **SERDP Thrust Area: Alternate/Clean Energy**

### **Title: Fuel Cells for Military Applications**

#### **Problem Statement:**

The majority of central heat plants on U.S. military bases are nearing the end of their useful life and will soon need replacing. This presents an opportunity to replace existing equipment, based on energy concepts developed almost eighty years ago, with current state-of-the-art or near-term emerging technologies. Fuel cells are electrochemical power generators with the potential for attaining very high electrical energy conversion efficiencies while operating quietly with minimal polluting emissions. In addition, by-product thermal energy generated in the fuel cell is available for use for cogeneration of hot water or steam, bringing the overall potential conversion efficiency (electrical plus thermal) to the order of 85% to 89%. Phosphoric Acid Fuel Cells (PAFC) are currently entering the initial stages of commercialization. One U.S. manufacturer has reported 55 firm orders for 200-kW PAFCs. Of these, 25 have been delivered, but only 3 units have been installed in CONUS. Molten Carbonate (MCFC) and Solid Oxide (SOFC) fuel cells, offering even higher electrical energy conversion efficiencies and increased cogeneration utility, are expected to become commercially available around the turn of the century. The proposed project is a new program designed to provide a field demonstration of PAFC technology at several DoD military installations in CONUS.

#### **Project Description:**

The technical objective of this project is to demonstrate the performance of phosphoric acid fuel cell technology on U.S. military installations. The FY 93 Defense Appropriations Act provided \$6.0M of equipment procurement funds per service for "non-developmental item natural gas fuel cells currently produced in the United States...for power generation at military installations..." with the recommendation that "...some of the cells be installed at locations in need of enhanced air quality...". In a similar fashion, Congress also supplied \$865K to the U.S. EPA for "...environmental monitoring of...non-developmental natural gas fuel cells...installed for power generation at military installations...". The problem with these Congressional appropriations is that money was provided to buy fuel cells and to monitor the environmental emissions, but no money was supplied to identify demonstration sites, develop site specific designs, install the equipment and make connections to local utilities, or monitor equipment performance. To resolve these problems, the Defense Utilities and Energy Coordinating Council (DUECC) decided to conduct a unified demonstration of the emerging PAFC technology for each of the three services, and tasked the Army as the lead service for coordinating these demonstrations.

This SERDP project will develop application guidance for PAFC technology, recommend U.S. military installation demonstration sites to the DUECC, develop an implementation plan for conducting the tri-service PAFC demonstration at multiple military installations, develop the equipment purchase documentation, develop equipment installation procedures and designs, design inter-ties with local utility systems, monitor equipment performance (in conjunction with U.S. EPA environmental emissions monitoring), train maintenance personnel, resolve operations and maintenance problems, and develop lessons learned for future fuel cell

technology applications. Funds for implementing SERDP funded designs at specific installations will be supplied by the Energy Conservation Program (ECIP).

The combined electrical and thermal energy conversion efficiency of PAFC technology in a co-generation system is 85% to 89%. This is far superior to the conventional technologies which range between 50% to 59%. This improved efficiency will help DoD meet energy reduction goals. The extremely low air pollutant emissions associated with fuel cell technology is in direct support of DoD/DOE environmental objectives. Potential PAFC system air emissions for key pollutants (SO<sub>2</sub>, NO<sub>x</sub>, and particulates) are negligible and in orders of magnitude below any conventional technologies and the proposed New Source Performance Standards [NSPS] of the 1990 Clean Air Act. Because of their high energy conversion efficiency, fuel cell power plants also produce lower levels of greenhouse pollutants (such as carbon dioxide) as compare to conventional technologies.

The primary technical task with fuel cell technology is directly related to the lack of long term operating experience. The original DOE funded prototype PAFC system only has a total of 9600 operating hours spread over 33 operating periods. A second developmental system located at the South Coast Air Quality Management District office in the Los Angeles area has less than 4500 operating hours with the longest continuous operating period being about 2100 hours. Completion of the extensive Congressionally directed demonstration program will resolve many of the technical issues surrounding this emerging technology.

#### **Expected Payoff:**

Because the current capital cost of \$5000/kW is very high, initial applicability will probably be restricted to DoD installations located in air quality non-attainment regions. One such installation is Vandenberg AFB located in Santa Barbara, CA. Vandenberg uses diesel generators to supply hot backup electrical power for space vehicle launches. These diesel generators currently violate local air quality standards for NO<sub>2</sub> and VOC emissions. Use of a PAFC system should resolve this continuing violation problem. As production costs decrease, fuel cell technology should prove to be cost-effective based on electrical energy production costs alone. Current industrial projections predict mature market installed costs for PAFCs to be less than \$2000/kW. With expected natural gas prices at \$4.00/MBtu, these systems should be cost effective in any region in which electric energy costs exceed 3.5 cents/kWh, with thermal energy provided for free.

#### **Milestones:**

FY

Develop PAFC application guidance for DoD	93
Collect pertinent DoD energy consumption/cost data	93
Collect DoD environmental compliance data	93
Determine Utility Company leveraging opportunities	93
Develop PAFC implementation plan for DoD	93
Develop RFP for delivery of turnkey PAFC systems for DoD	93
Develop/implement PAFC performance test plan	94-95
Monitor PAFC purchase/installation process	94-95
Monitor PAFC system performance	95-96
Document PAFC program lessons learned	97

Apply PAFC program lessons learned to provide guidance for the potential application of advanced fuel cell technologies to DoD

95-98

#### **Transition Plan:**

Information and technology developed by this jointly funded demonstration program will be transferred to the public sector through DOE's Technology Transfer Program for Fuel Cell Applications conducted by DOE's Morgantown Energy Technology Center, and to the DoD user community through a tri-service Technical Manual series. Technology improvements developed under this demonstration will be incorporated into the production process of the one commercial vendor who produces 200 kW PAFC units. The application guidelines, site specific design concepts, operational experience and lessons learned developed by this project will be extremely important to future users of PAFC, MCFC and SOFC technologies.

#### **Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
R&D Program	70	100
R&D Energy Office	145	
U.S. EPA R&D	285	435
FY93 Appr. Act	6000	9000
DoD ECIP		1200
SERDP	<u>350</u>	<u>350</u>
Totals:	6850	11085

#### **Performers:**

The extensive experience of DOE's Morgantown Energy Technology Center (METC), the Gas Research Institute (GRI), the U.S. EPA's Air and Energy Engineering Research Laboratory (AEERL) and the U.S. Army's Construction Engineering Research Laboratories (USACERL) will be extensively involved in this program. Local installation engineering and operations staff, and regional U.S. Army Corps of Engineers District offices and U.S. Navy Engineering Field Division offices will be involved at specific demonstration sites. DoD and DOE research contractors who have demonstrated expertise in the fuel cell technology arena will also be employed during the program. Selection of the candidate PAFC demonstration sites as part of the implementation plan will be coordinated among the Tri Services. Potential leveraging opportunities available as part of existing or negotiable incentive plans offered by local gas and electric utility companies will be identified and incorporated into the project where applicable. Overall project oversight will be provided by the Defense Utility Energy Coordinating Council (DUECC).

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**SERDP Thrust Area:** Alternate/Clean Energy

**Title:** Low Energy Model Installation Program

**Problem Statement:**

Defense Energy Program Policy Memorandum (DEPPM) 91-2 requires DoD facilities to reduce energy consumption and costs by 20% from 1985 to 2000, by improved operation and maintenance, capital investment for energy conservation, taking advantage of public utility and demand side management (DSM) programs, using shared energy savings contracting, using efficient lighting systems, and switching to alternative, renewable, and clean energy. The recently signed Energy Policy Act requires that all projects that payback within ten years be completed by 2005. The proper analytical tools and methodologies to enhance and ensure implementation of the energy program are not available. The DoD also has no tried and proven example that all the strategies can be simultaneously implemented utilizing existing resources available to the DEH community. The DoD Low Energy Model Installation Program at Fort Hood, Texas, will meet the goal of demonstrating the effectiveness of a comprehensive approach and allow development and technical transfer of tools and methodologies. Phase I and Phase II SERDP, DoD and FORSCOM funding have enabled the program to be initiated. Continued funding is required to enhance generic tool development and construction design enhancement methodologies, design projects and complete demonstration projects at Fort Hood, the model installation.

**Project Description:**

The continuing technical objective to demonstrate a prototypical installation-wide, comprehensive energy management program that improves the environmental compliance status of DoD installation utility and industrial systems while meeting DoD energy management goals to reduce usage and costs by 20%. Fort Hood, located in Killeen, Texas, has been selected as the model prototype installation for implementation of the required strategies for meeting these goals and quantification of the environmental compliance benefits resulting from energy management. Implementation procedures and tools are under development, in conjunction with DOE labs, that will enhance analysis techniques and demonstrate the effectiveness of a comprehensive, coordinated program based on state-of-the-art technologies and alternative funding strategies.

The program's technical approach includes:

- (1) a procedure for tracking and predicting installation energy use
- (2) a procedure for evaluating the efficacy of vegetation screening systems
- (3) a method for identifying and evaluating energy reduction options
- (4) a technique for prioritizing and funding options
- (5) a procedure for quantifying environmental benefits
- (6) a procedure for developing phased implementation plans

The program builds upon and enhances previous work by Pacific Northwest Labs in the development of the Federal Energy Decision Screening Model (FEDS) and the previous work by Lawrence Berkeley Labs in the development of End-use Disaggregation Algorithm (EDA). It also compliments the separately funded CERL work effort to develop the Renewables and

Energy Efficiency Planning (REEP) model to determine the maximum potential and the environmental benefits of energy conservation in the DoD.

#### **Expected Payoff:**

Fort Hood spends about \$23 million per year for facilities energy. Preliminary analysis of the potential savings at the model installation are about 32% of the energy and 24% of the costs. Since the Army spends about \$1.2 billion per year for facilities energy, savings of this magnitude extrapolated Army-wide are about \$288 million per year. There are also considerable environmental benefits from such energy reductions. Developing the analysis techniques and user friendly tools for energy analysis and capital investment strategies will enable installations to develop the cost effective projects to achieve there potential savings maximizing the use of alternative financing.

#### **Milestones:**

Select and evaluate demonstration site	FY92 (cmpl)
Evaluate energy use patterns	FY93
Develop energy tracking and prediction model	FY93
Identify and evaluate conservation projects	FY93
Develop tools for identifying options	FY92-94
Develop energy project strategy and plans	FY93
Evaluate the impact of vegetation screens	FY94
Conduct DSM negotiations	FY92-93
Develop project documents	FY92-94
Design Projects	FY93-95
Follow construction and evaluate projects	FY93-96
Evaluate results and transfer technology	FY93-96

#### **Transition Plan:**

The results of this program are twofold. The first area is in tool and technique development. These will be transferred within the existing structure for energy management within the DoD. The militarized version of FEDS will be incorporated into DOE's training program and the predictor tools and analysis techniques will be incorporated into DoD training programs. The second area of results are the actual demonstrations at the model installation. These projects will fully involve the installation, the local CoE district, and the various Corps Centers of Expertise. These results will be transferred using standard DoD methods such as technical reports, manuals, and notes. They will also be incorporated into training associated with the energy management programs. The technologies being implemented under this program are readily available from industry but have not penetrated the DoD market.

#### **Funding: (\$M)**

	<b>FY91</b>	<b>FY92</b>	<b>FY93</b>	<b>FY94</b>
SERDP	1.75	0.74	1.4	1.3
DoD	0	0.3	0	5.0
FORSCOM	0.2	0.3	7.0	7.0



**Performers:**

This project is being managed and performed by the Construction Engineering Research Laboratories in Champaign, IL. Additional assistance is being provided the Cold Regions Research and Engineering Laboratory in Hanover, NH; National Labs (PNL and LBL); various consulting and engineering firms. Huntsville and South Central Divisions of the Corps of Engineers are also program partners.

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**SERDP Thrust Area:** Alternate/Clean Energy

**Title:** Geothermal Heat Pumps/Enhanced Building Envelopes

**Problem Statement:**

The goal is to develop permanent DoD capability to evaluate, install and maintain geothermal heat pumps (GHPS) to reduce electric energy consumption for heating, cooling and water heating by \$100 to 150 million annually by the year 2000.

As a result of technological advancements, reduced GHP installation costs, and utility rebates, GHPs are increasingly installed in all sizes of new buildings as well as retrofits. Expands the initial SERDP funding, primarily for residential buildings, to include large DoD buildings; includes building envelope enhancements to further reduce energy consumption, atmospheric emissions, and life cycle costs for GHP installations.

**Project Description:**

The technical objective is to validate and document reduced energy usage, lower emissions and maintenance savings for DoD buildings, obtain load reduction data for DoD and the utility industry, and incorporate GHP design specifications in DoD engineering analysis for new or replacement HVAC designs.

The technical approach will be to rank larger DoD buildings for cost, energy, emission and maintenance reduction via geothermal heating; cooling, and water heating, select a number of sites for detailed economic analysis and engineering; incorporate GHP analysis in DoD HVAC computer models; and develop a permanent DoD program to extend the technology for both new and retrofit HVAC needs. Where cost-effective, incorporate building envelope enhancements to further reduce energy consumption.

DOE and EPA have both endorsed GHP technology to reduce energy consumption and power plant emissions. "GHPs can reduce energy consumption and, correspondingly, emissions by 34-46% compared with the most advanced air source heat pumps, and by 71-73% compared to electric resistance coupled with standard air conditioning equipment. Total U.S. market demand for GHPs could increase from present sales levels of 20,000 units annually to over 450,000 by the year 2000 with aggressive utility conservation incentives." (U.S. EPA July 1992). Exclusive of liquid fuels, GHPs are the most promising dispersed renewable technology, with a potential of 2.7 quads by 2030 up from less than .1 quad in 1990. This estimate was based on assumed simple paybacks of less than 5 years for commercial applications and less than 8 years for residential installations. (Energy Information Administration, DOE, December 1990).

This phase enhances a previously funded SERDP GHP program which was developed primarily for DoD residential buildings. DoE GHP R&D seeks to lower installation of ground connections, EPA is developing utility load models for GHPs, and Farmers Home Administration installs GHPs in low income housing because of its most favorable life cycle cost.

**Expected Payoff:**

The GHP technology is cost-effective nationwide. DoD's total U.S. electric bill for heating, cooling, and water heating is about \$700 million annually. The potential annual savings for both residential and commercial DoD type buildings is estimated at \$140 million by the year 2000.

**Milestones:**

1. Identify 12 DoD residential sites	February 1993
2. Identify 6 DoD large building sites	March 1993
3. Conduct National GHP teleconference for A&E firms	April 1993
4. Train DoD personnel	May 1993
5. Assist preliminary engineering & cost analysis (residential)	July 1 1993
6. Assist preliminary engineering & cost analysis (large)	September 1993
7. Complete residential construction	January 1994
8. Complete large building construction or retrofit	August 1994
9. Document energy, emissions, and maintenance savings	July 1995
10. Complete report	December 1995

**Transition Plan:**

After this 3 year program, DoD will have incorporated GHPs in its design process. This project is being coordinated with DoD's Defense Utility Energy Coordinating Council, including both the operations and maintenance and the utility/DSM subcommittees. The GHP manufacturers, small by traditional HVAC standards, are being joined by the larger manufacturers like Trane-Consequently, equipment production is assured by the existence of a burgeoning civilian GHP market.

**Funding: (\$K)**

FY 93  
600

**Performers:**

DoD/DOE/Sandia Laboratories: Albuquerque NM; Oklahoma State University; Louisiana State University; and University of Kentucky

International Ground Source Heat Pump Association had agreed to cooperate with DoD, nationwide.

Planned Cooperative Development Agreements will coordinate with the Electric Power Research Institute and National Rural Electric Cooperative Association, both of which play prominent roles in accelerating adoption of GHP technology.

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**SERDP Thrust Area:** Alternate/Clean Energy

**Title:** Advanced Cycle Mobile Heat Pump

**Problem Statement:**

The goal of this project is to develop new energy-efficient field-deployable environmental control units (ECU). By utilizing new technology in the thermodynamics field, new heat-pump cycles can be applied that allow cooling without using the ozone-depleting CFCs that normally occur in the cooling cycle.

Global goals have been established to reduce and eliminate the use of CFCs due to the global warming issue. Federal regulations require that certain CFCs be phased out by 1995. To accomplish this, new cooling technologies must be explored.

**Project Description:**

The technical objective is to develop a thermoacoustic heat pump to provide a bare base with highly efficient, low maintenance heating, ventilating and air conditioning (HVAC) systems.

The technical approach will be to utilize traditional heat engine cycles, such as the Carnot cycle, which have been used in the past with the assumption that the cycle was a reversible function. There are limiting values never realized in practical heat engines due to the unavoidable irreversibility, such as thermal diffusion and viscous dissipation, which always reduce performance below the ideal Carnot values. In thermoacoustic engines, the irreversibility is due to the imperfect (diffusive) thermal contact between the acoustically working fluid and a stationary second thermodynamic medium that provides the required phasing. This project will develop a computer model to optimize a thermoacoustic heat pump on the basis of resonance and system size. The computer model will consider the cost effectiveness and identify the optimum thermoacoustic configuration for a prototype model. The prototype will be fabricated to validate the practicality of a working heat pump to meet bare base requirements. The resulting configuration will be tested and its performance data compared with current systems to determine the cost effectiveness of the new equipment.

This effort will eliminate the use of CFCs on deployable heat pumps and provide a more energy efficient method for heating and cooling. This will reduce the amount of fuel needed to meet requirements.

**Expected Payoff:**

The research, development of this advanced energy conversion technology will increase operations efficiency and eliminate the use of CFCs as operational media. Clean ECU are essential for successful mission operations and sortie generation. Efficient resource utilization will result in significant cost and cleaner environmental benefits.

**Milestones:**

Start Program	FY93
Literature/Technology Review	FY93-FY94
Computer Mode	FY93-FY95
Thermodynamic Cycle Analysis	FY94-FY95
Energy/Economic Optimization Analysis	FY95-FY96
Small Scale Testing	FY95-FY97

**Transition Plan:**

The results of this R&D will be transitioned to Wright Laboratory Flight Dynamic Air Base System (FIVC) 6.3 operational prototype validation program. This will support base civil engineers requirement to use environmentally friendly cooling media.

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
500	950

**Performers:**

Department/Agency Laboratory: US Air Force, Wright Laboratory Flight Dynamic Air Base System (FIVC). Planned Cooperative Agreements: None

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## **SERDP Thrust Area: Alternate/Clean Energy**

### **Title: Utilization of Biomass Technologies on Military Installations**

#### **Problem Statement:**

The goal of this is to demonstrate an innovative energy conversion technology fueled with biomass at a DoD installation. The DoD operates a large number of small energy conversion systems that burn fossil fuels and are in need of repair or replacement. These systems emit substantial amounts of air pollutants (SO<sub>2</sub> and particulate) which must be controlled. Converting or replacing existing equipment with systems that utilize biomass would eliminate SO<sub>2</sub>, produce zero net gain of CO<sub>2</sub>, reduce air toxic emissions, and reduce waste disposal problems. The biomass fuel supply would be generated by activities on-site, in the community, and/or from dedicated feedstock supply systems (DFSS). This project is an opportunity for the DoD, EPA, DOE, USDA, AID, national labs, and industry to cooperate in demonstrations that will benefit each organization. The project would build upon the EPA/OPPE and DoD study "Enhancing Management of Forests and Vegetation on Department of Defense Lands: Opportunities, Benefits, and Feasibility", the EPA/AEERL, DOE, and AID biomass integrated gasification/gas turbine study, the USDA work with a wood fired combustion turbine, utilization of wood pallets and marketing of cull trees, the NREL gasifier scale-up in Hawaii, the Western Research Institute work with co-firing wood and coal in a turbine, the Regional Biomass Program utilization of biomass, the EPA/AEERL multi-fuel combustor research, and ORNL research in DFSS. Existing efforts have focused on large scale systems or mature technologies. The small scale innovative energy conversion technologies have been neglected.

#### **Project Description:**

The technical objective of this project is to demonstrate that innovative energy conversion technologies fueled with biomass are technically, economically, and environmentally feasible for DoD installations, industries, and developed countries. The technical approach is to identify the DoD site, select the most viable technology, identify the partners, and design, build, and test the system. The DoD/CERL (Gary Schanche) would provide the demonstration site, specific information to aid the technology selection process, and system operators. The EPA/AEERL (Carol Purvis) will select technologies to be considered, evaluate environmental and site specific data, and coordinate project participant's activities. The DOE/NREL (Ralph Overend) would provide their expertise in the technology selection process. The Regional Biomass Programs, USDA (Andy Baker) and ORNL (Lynn Wright) would provide off-site resource information, including DFSS. Industry would provide system development/design and hardware depending on the technology selected. AID/Winrock would examine opportunities for transferring technology to international markets. The project relates to the needs of the DoD by supporting Pillar 3 of the Tri-Service Research Plan, Thrust 3.M: Reduce greenhouse gas emissions, (3.V.2.d) Improve efficiencies of mechanical systems and (3.V.3.a) Alternative/renewable energy sources and the DOE by supporting Title XII: Renewable Energy of Energy Policy Act of 1992, H.R. 776/Public Law 102-486, +direct combustion or gasification of biomass and +biofuels energy systems. The technical risks will be minimized by the proper selection of technology based on the available site, size of system, type of fuel, qualifications of operators, and lessons learned by all

cooperators.

### **Expected Payoff:**

Conversion technologies fueled with biomass could be applied in developed or developing countries, industrial sites, or rural areas. The technologies could be modularized to allow for varying fuel supplies or energy demand. The benefits for the DoD to convert or replace these systems with biomass fueled systems are 1) reduce air emissions, 2) minimize on-site and community waste disposal, 3) savings from tipping fees, purchase of fossil fuels, and electricity, 4) energy security at domestic and international military installations, and 5) promotion of exportable technologies.

### **Milestones:**

- |   |       |
|---|-------|
| - Identify available site(s), the existing system, and on-site fuel supply. | 04/93 |
| - Identify various technologies.  | 04/93 |
| - Identify off-site fuel supplies.  | 05/93 |
| - Select site(s).   | 06/93 |
| - Select appropriate technology(ies) for selected sites.                    | 08/93 |
| - Establish partnerships with government and industry.                      | 09/93 |
| - Define contributions and responsibilities of partners.                    | 10/93 |
| - Assist with design of system.   | 11/93 |
| - Begin demolition/construct of system.                                     | 01/94 |

### **Transition Plan:**

The coordination between DoD and partners will be such that the design of the project will be in the best interest of the DoD installation. This project would provide the jump start needed for the development of equipment, design of systems, and creation of markets. Biomass fueled technologies will help provide sustainable energy without being detrimental to the environment. The following is one example of a technology that could be demonstrated and the benefits. Energeo's system is a closed Brayton Cycle - a turbine using air as the working fluid which is heated via heat exchangers in a fluid-bed combustor. The benefits of this system are 1) less turbine maintenance because of air working fluid, 2) fuel flexibility because combustor and turbine are closed systems, 3) easily exportable because system is designed to fit in shipping containers, 4) small size (700kW) can be modularized, and 5) utilizes biomass. A successful demonstration would allow developing countries to get approval for financing from multi-lateral lenders. The potential systems will be comprised of off-the-shelf components or manufacturable by existing industries. Developing countries are in dire need of this type of technology because biomass waste is both a disposal and air pollution (open burning) problem and diesel fuel is too costly to import.

### **Funding:**

- SERDP would provide \$750,000 per year for FY93-96.
- DoD would provide the site and system operators.
- EPA/ORD would provide in-house multi-fuel combustor (\$500K) and staff operators



(\$250K) for fuel testing. In addition, approximately \$1M of a pending FY94 initiative for GHG emission reduction technologies would support this program.

- EPA/OPPE would add forest and agricultural sector to GEMINI U.S. energy sector model to assess biomass energy feasibility (\$100K) and perform analysis of large scale use of biomass in U.S. power sector (\$200K).

- TVA FY93 funding is temporarily frozen due to a reorganization but expect to be interested in co-funding in FY94.

- DOE and NREL FY93 funding is already committed but are prepared to consider the project for FY94 funding.

- NWEA will provide in-kind staff time in FY93 and are prepared to commit \$25,000 in FY94-96.

#### **Performers:**

Demonstration of energy conversion technologies utilizing biomass will be performed through the cooperation of the EPA, DoD, DOE, USDA, AID, national labs, and industries. This government/industry cooperation should lead to future CRADA's between government and industry.

#### **Primary Sponsor:**

Air and Energy Engineering Research Laboratory (AEERL)

Office of Research and Development

US Environmental Protection Agency (EPA)

MD-60

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**Co-Sponsors:** The following organizations have been contacted and agreed to be funding co-sponsors or partners who will at a minimum provide in-kind support.

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**SERDP Thrust Area:** Alternate/Clean Energy

**Title:** Pilot Plant Demonstration of Methanol Production using the Hydrocarb Process with Biomass Feedstock

**Problem Statement:**

The goal of this project is to demonstrate the feasibility of producing methanol from biomass using the Hydrocarb process with special emphasis on the recovery of a clean liquid fuel from abundantly available DoD biomass feedstocks.

Domestic supplies of petroleum are declining with adverse effects on national security and balance of payments. Because of this and other facts, the strategic energy plan of the Department of Energy anticipates that alternative fuel of some kind will be required in large amounts by the year 2000. The Department of Defense is a large consumer of transportation fuel and will increasingly compete with the private sector for available petroleum supplies. The necessary future transition to an alternative fuel can be facilitated by participation of DoD in the development of new technology to produce the best alternative from renewable domestic resources at lowest cost.

This project is an enhancement of an existing project jointly funded by the EPA (FY 92 = \$400K) and the California South Coast Air Quality Management District (FY 92 = \$125K) with the participation of the Brookhaven National Laboratory.

**Project Description:**

Preliminary engineering feasibility studies and cost estimates carried out under EPA sponsorship during 1990-92 indicate that the Hydrocarb process, which was conceived at the Brookhaven National Laboratory, may produce a clean liquid fuel from biomass at a cost lower than the equivalent cost of gasoline. Environmental effects, relative to gasoline emissions, will also be greatly reduced. Most importantly, the assessments conclude that it will yield more fuel from the given resources than any other technology. Those assessments are based on theoretical process simulations and laboratory rate studies conducted at Brookhaven. Pilot scale testing is now being undertaken in a joint project to further evaluate the process.

The technical approach is to design, construct, and operate over a three year period, a 100 gal/day pilot plant in four phases. The SERDP project would accelerate and enhance the construction of the second phase, a methane pyrolysis reactor, which is the critical component of the system. When completed, the pilot plant would demonstrate the recovery of clean fuel from wastes produced at military installations; e.g., rubber tires, discarded fabrics, spent organic wastes.

The Energy Policy Act of 1992 (P.L. 102-486) provides that the Department of Energy shall establish programs to promote replacement of petroleum motor fuels with alternative fuels to the maximum extent possible in order to ensure the availability of alternatives that will have greatest impact on reducing oil imports, improving national economy, and reducing greenhouse gas emission. The numerical goals are 10% of petroleum motor fuels with

alternative fuel by 2000, 30% by 2010. Pillar 3 of the DoD Environmental Research Plan (Pollution Prevention) THRUST 3.M: Reduce Greenhouse Gas Emissions is also directly supported by this project which will produce alternative/renewable energy sources (3.V.3.a) and eliminate/reduce hydrocarbon fuel use (3.V.2.b). The Hydrocarb process will reduce greenhouse gas emissions by 67% relative to the gasoline displaced and at no incremental cost.

Four other biomass gasification processes that could produce methanol from biomass and three processes that could produce ethanol from biomass have been compared with the projected performance of this process. These evaluations indicate that Hydrocarb could produce over 4 times as much fuel energy from a given amount of biomass, and at less cost, than the most advanced processes now under development for production of fuel ethanol and could produce 3 times as much methanol as any gasification process. Cost of fuel production will be significantly less than either of those alternative routes.

Process simulation and optimization studies, laboratory rate studies and pilot plant conceptual design have been completed. Design of a hydrogasification reactor is complete and construction will begin in January. Design of the second unit, a methane pyrolysis reactor will be undertaken in October. Gasification tests will begin in December. The second year will involve testing of the gasification and pyrolysis units and installation of the methanol synthesis unit. The integrated system will be evaluated in the third year.

Most of the involved process steps have been carried out independently on industrial scale, but not at the specific temperatures and pressures needed for this process. The methane pyrolysis unit, which involves high temperature indirect heating by a pressurized combustor, will require development.

#### **Expected Payoff:**

If successfully developed, the Hydrocarb process could provide a large part of the fuel requirements for military use, from secure domestic resources, as well as a large part of the transportation fuel requirements of the U.S. public. The total U.S. land area that could be used for short-rotation woody biomass farming is estimated to be capable of producing 6 to 12 quads of energy. Because Hydrocarb could produce methanol in amounts equivalent to twice the gross energy content of the biomass, it could potentially supply two thirds of the transportation energy requirements of the U.S. If one-third of that requirement could be met with domestic methanol and the minimum estimated external costs of petroleum fuel dependence is included, an annual saving of \$25 billion would result.

#### **Milestones:**

Phase 1

Phases 2 and 3

- Gasifier construction

- Gasifier operation

- Pyrolyzer design

- Pyrolyzer construction

- Pyrolyzer operation

- Methanol unit plant

#### Phase 4

Methanol unit construction  
Integrated plant operation

#### Transition Plan:

The test unit is the smallest system that could provide useful information on the potential of the process. If successful, evaluation on a process development unit (10 tons/day) and a process engineering unit (100 or more tons/day) will be needed for final scaleup and accurate assessment of performance and cost. It is clear that the private sector has no current incentive to develop methanol as an alternative to petroleum --the true cost of which is heavily subsidized by the public sector. It is essential therefore, if the best alternative is to be made available by year 2000, that process development begin now. Support by DoD for the initial development phase of this process should enhance the prospects for a secure supply of its fuel requirements as well as assisting the public and private sectors with the development of technology to meet the future needs of both. A successful pilot demonstration with DoD support will greatly improve the prospects of early support by the petroleum industry for scaleup and evaluation in larger systems.

#### Funding:

FY92 EPA \$400K

South Coast Air Quality Management District (SCAQMD) \$125K  
Brookhaven National Laboratory (BNL) \$50K in-kind staff time

FY93 EPA \$120K

SCAQMD \$375K

SERDP \$500K

BNL \$50K

Center for Emissions Research and Analysis (CERA) \$6K

FY94 EPA \$250K

SCAQMD \$250K

SERDP \$500K

BNL \$50K

CERA 12.5K

**Performers:**

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## Compliance

Project Title	Page Number	Funding FY93 (K)
Maintenance Process Emissions		
Steady-state and Nonsteady-state Source NO <sub>x</sub> Emission Control (AF)	37	1,000
Combination Sorption/Catalyst Medium for Destruction of Halogenated VOCs - Dover Air Force Base (EPA)	41	500
Atmospheric Chemistry of Model AF Pollutant Compounds (AF)	45	255
Manufacturing and Disposal Emissions		
Encapsulation of Hazardous Ions in Smectite Clays (DOE)	47	352
Fundamental Studies of Hazardous Metal-Ion Separations Chemistry (DOE)	53	450
Dispersion in the Convective Boundary Layer (EPA)	57	200
Fundamental Studies of Thermal, Plasma, and Photochemical Processing for Waste Disposal Applications (A)	59	350
Energy Conservation and Air Toxic Compliance Plan for DoD Industrial Facilities (A)	62	550
Supercritical Water Oxidation of Hazardous Waste (N)	65	900
Kinetic Mechanisms for Supercritical Water Oxidation (DOE)	72	490
Open-Burning/Open Detonation of Explosives		
Advanced Testing of Emissions Produced During Open-Air Destruction of Energetic Materials (A)	76	568
Solar Detoxification of Explosives in Water (DOE)	79	890
Hydrothermal Reduction of Eroded and Intact Energetic Wastes (AF)	85	390
Catalytic Extraction Processing of Energetic Wastes and Munitions (A)	90	600

Project Title	Page Number	Funding FY93 (K)
Operations and Training Emissions		
ADVACATE Boiler Emission Control System (EPA)	94	1,250
e-SCRUB - The Application of DNA Pulsed Power to Electron Scrubbing of Flue Gas to Remove Unwanted By-products (DNA) *	98	833
Ship Emissions		
Shipboard Non-Oily Wastewater Treatment System (N)	101	1,325
Noise Impact Assessment		
Single Event Noise Exposure/Development and Human Response Prediction Model (AF)	105	350
Turbulent Boundary Layer Effects on Sound Propagation (A)	109	175
Small Arms Range Noise Mitigation Technology Demonstration (A)	111	100
Shore Management of Ship Wastes		
Contaminant Dispersal Model for San Diego Bay (N)	114	690
General Hazardous Waste Management		
Portland-Cement Concrete Liners and Tanks for Isolating Hazardous Wastes (A)	119	90
Capacitive Deionization as a Means of Eliminating Secondary Wastes (DOE)	121	795
Glassy Materials Modeling for Hazardous Waste Immobilization (A)	124	150
Waste Tank Remediation: Analysis and Waste Form Development (DOE)	126	217
Technical and Economic Assessment of Storage of Industrial Waste on Abyssal Plains (N) *	131	1,500
Total		14,970

\* Congressional Interest Program



## **SERDP Thrust Area: Compliance**

### **Title: Steady-state and Nonsteady-state Source NO<sub>x</sub> Emission Control**

#### **Problem Statement:**

The goal of this project is to define the practical limits to which reactive sorbent technical based on vermiculite and a coating of magnesium oxide (MgO) on vermiculite can be applied to control oxides of nitrogen (NO<sub>x</sub>) in combustion and other process exhaust streams. NO<sub>x</sub> emissions from stationary and mobile sources are or shortly will be subject to regulation under titles II, IV, and VII of the Clean Air Act Amendments of 1990 (CAAA), and EPA's Office of Air Quality Planning and Standards (OAQPS) is presently gathering data to support a set of regulations to be applied to jet engine test cells (JETCs).

Targeted department/organization: Air Force major command operations and maintenance activities that emit combustion exhausts, other DoD operations and maintenance activities, and private sector industrial operations will benefit from this research.

NO<sub>x</sub>--VOC interactions have been implicated in tropospheric ozone formation. Accordingly, effective atmospheric protection strategies require control of both NO<sub>x</sub> and volatile organic compounds (VOCs). Present-generation NO<sub>x</sub>-control methods are effective only on relatively constant ("steady state") sources of NO<sub>x</sub>. The vermiculite--MgO sorbent was developed to address the need to control NO<sub>x</sub> emitted from JETCs, which operate in a series of short stages, drastically removed from steady state, and which cannot tolerate more than an inch (water gauge) of back pressure from a control device. Bench- and prototype-scale tests indicate that NO<sub>x</sub> removal by this sorbent is practically constant over a temperature range exceeding 100° and over a range of space velocities exceeding a factor of 10, that approximately 60% of NO<sub>x</sub> (and comparable amounts of carbon monoxide [CO] and particulate matter) is removed, and that back pressure at the flow rates encountered in two JETCs is approximately 5 inches (water gauge). Extrapolation to full scale gives an estimated cost of \$4.50 per pound (for the JETC at SMALC/LABHCE, McClellan AFB CA), well within the criterion for cost effectiveness applied by OAQPS, and a standard of 50% removal is likely to be set in 1994 on the basis of this extrapolation. Design modifications have been proposed that should decrease back pressure to a nominal zero value, but it is untested at present and we have not shown on full scale that these sorbents can be used as a practical NO<sub>x</sub> control device. Unless the construction and evaluation here proposed is accomplished before OAQPS issues its standards, DoD is at risk of facing a regulation for which no technology exists.

Because the vermiculite--MgO sorbent is inexpensive and nonhazardous, and because its spent form is regenerable or disposable (as a nonhazardous waste) as a beneficial soil amendment, it has potential for application to a spectrum of steady-state sources as well. Concurrent evaluation for steady-state and nonsteady-state applications at a single site offers significant economies by sharing personnel and analytical facilities.

The mechanism of NO<sub>x</sub> removal by MgO coated on vermiculite appears to derive from distortion of the MgO structure, which allows metathesis and oxidation to form Mg(NO<sub>3</sub>)<sub>2</sub> at or near the surface. The kinetics of this process and the influence of ethylene (selected as a

representative hydrocarbon contaminant) on the kinetics are the subject of a dissertation at U of Florida, on which work will begin during FY 93. A second dissertation, to be supported concurrently at Penn State U as part of this project, will examine the kinetics of reaction of NO, NO<sub>2</sub>, and CO in the presence of uncoated vermiculite. Taken together, these two studies will provide a sound experimental basis for designing applications of vermiculite/vermiculite-MgO technology. This is a new project.

### **Project Description:**

The principal technical objective of this project is use the engineering platform of a full-scale installation on an operating JETC to work out the technical details needed to prepare a generic design for a NO<sub>x</sub> control for JETCs (or, in the worst case, to establish definitively that this approach is incompatible with JETCs before OAQPS specifies it as Best Available Control Technology.) The secondary objective is to gather performance and cost data (including disposal of spent sorbent) for applications to a representative spectrum of steady-state sources: a field incinerator for spill remediation, a boiler, a bank of diesel generators, and tailpipe emissions from gasoline and diesel vehicle engines. The latter will be used in cost-benefit comparisons with established control technologies.

My two graduate students will operate independently of the site construction, working out the kinetics and mechanism of action of uncoated and MgO-coated vermiculite on NO<sub>x</sub> and on elementary, reducible carbon species. A control system will be designed for and installed on JETC#2, McClellan AFB, California (or another AFMC center if McClellan is selected for closure). This system will be refined and modified as an engineering test bed until satisfactory removal efficiencies are observed at back pressures low enough (a criterion to be experimentally determined) to permit "normal" operation of the cell, and until the sensitivity of the system--JETC interaction to variations in working conditions is understood. A modular emission control device will be designed and installed, in turn, on the stacks of an incinerator at a hazardous spill site, a boiler, and a bank of diesel electric power generators. Such variables as bed area and thickness will be examined to determine "best" treatment conditions (for each stack), and removal and cost data will be gathered. A tailpipe-size unit (backed up to a mechanical filter or a precipitator to prevent contamination of the vermiculite bed by soot and metal particulates) will be assembled and refined on an automobile exhaust pipe in a garage. After satisfactory operating characteristics are established, the unit will be road tested on a gasoline powered vehicle (to determine effect on performance and ruggedness of the unit) and then on a diesel-powered vehicle. Sorbent used in each stage of testing will be analyzed carefully to determine the extent of contamination, if any, by heavy metals, which will determine disposability.

Relationship to DoD environmental objectives: This research directly contributes to the requirement to control maintenance process emissions as identified in the Tri-Service Environmental Quality Strategic Plan, DoD Pillar 2: COMPLIANCE; Requirement thrust 2.B.2: Maintenance Process Emissions (Test Stands and Cells). It also addresses California requirements for reduction of NO<sub>x</sub> emissions from fixed and mobile sources.

This is a continuation of a Small Business Innovation Research (SBIR) program that began with seven independent approaches to No<sub>x</sub> control for JETs. Six were dropped as impractical or cost-ineffective at their present state of development, and the sorbent concept

was carried to the limit allowed by SBIR rules. (A thesis underway at Cal Irvine is examining the effect of mixing efficiency on the rate and extent of NO<sub>x</sub> removal by the Thermal DeNO<sub>x</sub> process, but the temperature requirements for DeNO<sub>x</sub> treatment are incompatible with temperature distributions in the augments tube of a JETC.) Two new SBIR contracts will explore alternative approaches to NO<sub>x</sub> control for JETCs, but will take several years to deliver a workable product in the best of circumstances.

There are a few limited risks. Sensitivity to even minimal back pressure may prevent treatment of JETC exhausts by this method. Leakage from JETC during high-flow operation (afterburner) may exceed limits acceptable to EPA. Metal accumulation in the sorbent may convert it into a hazardous waste in an impractically short amount of time. (Pretreatment by filtration or precipitation should control the accumulation of particulates from steady-state and mobile sources; it is incompatible with the JETC.) The sorbent may not be as cost-effective as existing control methods.

#### **Expected Payoff:**

For JETCs, this effort will provide definitive information to guide the design and implementation of the only control technology that is presently able to meet incoming (FY 94) standards for NO<sub>x</sub> emission control. Return on Investment (ROI) is ability to continue operating facility, realized immediately. For vehicles, this effort will provide a tailpipe emission control capability for NO<sub>x</sub>, CO, and (possibly) hydrocarbons that uses no noble or heavy metals and that can be disposed as a nonhazardous waste. Assuming implementation at once, ROI also very short because NO<sub>x</sub> reduction credit for mobile sources will lessen pressure against other sources. For stationary steady-state sources, this effort will provide a competitive alternative to present methods of stack NO<sub>x</sub> and CO emission control that will have to be evaluated from data generated in this and other studies on a case-by-case basis. ROI estimated at 7.9 years.

**Milestones:** Following is the schedule of tasks/activities:

Complete Detailed Design for JETC; Stack testing at Site	DOA + 60 days
Assemble Bench-Scale Rig for Tailpipe Tests	DOA + 120 days
Prepare Sorbent	DOA + 180 days
Design for Stack Control	DOA + 180 days
Garage testing of Prototype Tailpipe Control	DOA + 240 days
Fabricate JETC, Stack Controls	DOA + 270 days
Installations on JETC, Incinerator	DOA + 360 days
Road Testing of Prototype Tailpipe Control on Automobile	DOA + 360 days
Reinstall Control on Diesel Bank	DOA + 450 days
Dissertations (Final Reports) on Mechanisms of Action	DOA + 480 days

Road Testing of Prototype Tailpipe Control on Diesel Truck	DOA + 480 days
Test Data from JETC	DOA + 540 days
Reinstall Control on Boiler	DOA + 630 days
Detailed Evaluation of Disposability/Recoverability of Sorbents	DOA + 720 days
Performance and Case Analysis	DOA + 780 days
Final Report	DOA + 840 days

The Air Force Center for Environmental Excellence's Technology Transition Division and the Control Technology Center at EPA Air and Energy Engineering Laboratory will be continually advised of the status of this research and will assist in the transition throughout the Air Force, other federal agencies, and the private sector. EPA-OAQPS will be updated regularly on progress on the JETC control, and will likely rely heavily on that information to guide the final definition of regulated standards.

**Funding: (\$K)**

SERDP 6.3	<b>FY93</b>	<b>FY94</b>	<b>TOTAL</b>
	1000	800	1800

**Performers:**

Primary AF POC: AL/EQS, Dr. Joe Wander (904) 283-6240/FAX 283-6286/6090.

Performing organization: Sorbent technologies Corporation (Twinsburg OH) or similar contract source that can provide needed ideas and expertise.

Planned cooperative/coordinating agencies: EPA-OAQPS

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**SERDP Thrust Area: Compliance**

**Title:** Combination Sorption/Catalyst Medium for Destruction of Halogenated VOCs - Dover Air Force Base

**Problem Statement:**

The goal of this project is to continue development, evaluation and optimization of an innovative adsorbing catalyst which will be pilot tested at the Dover Delaware Air Force Base as an alternative low-cost approach for eliminating Trichloroethylene (TCE) air emissions which occur during waste water cleaning operations. The US EPA Air and Energy Engineering Research Laboratory (AEERL) has sponsored research cooperatively with the Air Force to develop and optimize a single medium which first will act as a sorbent to remove low concentration VOCs at room temperature and then act as a catalyst at about 350°C to destroy the VOC.

The Y-Zeolites used as the base for the Zeolite/Transition Metal Oxide catalysts can be treated to have both high adsorption capacity and maintain their effectiveness in deep oxidation of chlorinated VOCs. Normally the catalyst would adsorb the VOC; but on regeneration cycles, heating the VOC would initiate its reaction as well as the desorption and reaction of the adsorbed VOCs. The project will expand the zeolite-transition metal oxide (TMO) catalysts developed with the University of Akron. These catalytic systems have the high activity, selectivity, and thermal stability necessary to effectively and economically destroy chlorinated hydrocarbons in dilute, humid VOC streams such as those at Dover Air Force Base.

This project is an enhancement to an existing SERDP project. \$300K of Phase I SERDP funds were received in FY92 to augment the existing EPA efforts described above.

**Project Description:**

The previous research sponsored by EPA identified the important requirements that such a catalytic system must have. These are (1) low maintenance expense, (2) low initial cost, (3) low pressure drop, and (4) low operating temperature. The benefits of the development of such systems were broad and have lead to new approaches on how they can be applied to the control of emissions of higher concentration chlorinated hydrocarbons and of other halogenated and substituted hydrocarbons, which are generally toxic in nature; and to the control of other volatile organic compounds which contribute to the ozone non-attainment problem or stratospheric ozone depletion problem.

The technical objective is to destroy halogenated VOCs contained in dilute, humid, and high volume streams such as those at Dover AFB without continuously heating this high volume stream to the 350°C to 500°C range. Initially sorbent/catalyst medium will adsorb the VOCs. The stream and bed will then be heated to initiate the catalytic reaction. Tremendous energy savings will result from only having to heat this stream on a part-time basis. This adsorption-reaction technique avoids the use of parallel beds and permits long unattended adsorption cycles followed by short desorption/reaction cycles. The low pressure drop associated with these high surface area supported zeolite monoliths would significantly lower

treatment costs of dilute, high flow streams such as those at Dover.

AEERL working cooperatively with the Air Force will evaluate the applicability of the innovative absorbing catalyst as a control technology for TCE air streams at Dover AFB. Laboratory testing and pilot scale field tests will be conducted to further optimize the adsorption capabilities of the Y-Zeolites and evaluate their performance on actual contaminated air streams.

This work will directly support a waste water cleanup effort at Dover Delaware Air Force Base. The emphasis of this cleanup is to eliminate air emissions of a two carbon halogenated VOC (TCE). This project will support cleanup of single carbon halogenated VOCs (carbon tetrachloride and methylene chloride) at the Hanford and Savannah River DoE sites. This research also supports Thrust 2.C.2 (Disposal Operations) of the Tri Service Environmental R&D strategy which includes a section (2.I.1.b) on controlling VOC air emissions from industrial waste treatment processes.

The additional FY93 SERDP funding will accelerate the development of these advanced adsorbing catalysts and will provide the opportunity to demonstrate their capabilities at additional sites and for different applications. This further development will improve the adsorption capabilities of the Zeolites and bring them to the commercialization stage more quickly.

Tasks for this project include the characterization of sorbent capacities of present catalysts, characterization of heat effects in present catalysts, and development of new sorbent/catalyst systems. Tests for new sorbent/catalyst and design calculations for sorbent/catalyst reactor system would be produced as well as a guidance method for initial pilot/field test. Additionally, construction and testing of new sorbent/catalyst reactor system and a guidance method for second pilot/field test must be conducted. Lastly, tasks must be scheduled for catalyst deactivation runs, scale-up and economic calculations, and guidance for final pilot/field test.

The two major technical issues are (1) finding a sorbent that is also catalytically active and (2) controlling the desorption reaction without excessive heat effects (catalyst deactivation).

This a continuation of SERDP Phase I work being performed under a Cooperative Agreement with the University of Akron entitled "Development of New Catalytic Methods for Destruction or Transformation of Halogenated VOCs".

#### **Expected Payoff:**

In addition to assisting Dover AFB address their TCE emissions, this research will support cleanup activities at other DoD, DoE, and industrial sites. This technique can also be applied to both large and small (e.g., dry cleaners) air sources of halogenated VOCs.

This additional SERDP funds will speed up efforts to optimize the adsorption capability of the zeolite based compounds thereby enhancing renewal efficiency.

**Milestones:**

Award of new Cooperative Agreement	FY92
Expand characterization of sorbent capacities of present catalysts	FY93
Expand characterization of heat effects in present catalysts	FY93
Expand development of new sorbent/catalyst systems	FY94
Expand tests for new sorbent/catalyst	FY94
Accelerate design calculations for sorbent/catalyst reactor system	FY94
Provide Guidance for Initial Pilot/Field Test	FY94
Expand construction of new sorbent/catalyst reactor system	FY94
Submit expanded Phase I Report	FY94
Test new sorbent catalyst reactor system	FY95
Provide Guidance for Second Pilot/Field Test	FY95
Carry out catalyst deactivation runs	FY95
Make scale-up and economic calculations	FY95
Provide Guidance for Final Pilot/Field Test	FY95
Submit Final Report	FY95

**Transition Plan:**

Battelle Columbus, the contractor for U.S. Air Force (USAF), is working with the University of Akron Principal Investigator, Dr. Howard Greene. A zeolite/TMO catalyst was developed under the previous Cooperative Agreement in support of an Interagency Agreement (IAG) with the Air Force. Dr. Greene will supply this catalyst and the sorbent/catalysts developed under this work to Battelle. In addition, Dr. Greene and the EPA Project Officer will coordinate with Captain Edward Marchant (USAF), John Steele (DoE Manager of Waste and Environmental Remediation for Westinghouse Savannah River Lab), and Steve Stein (Battelle contractor for Hanford).

**Funding: (\$K)**

FY92	FY93	FY94
300	500	500

In addition to these SERDP funds, the Air Force has also contributed substantial resources over the last three years towards this effort.

**Performers:**

This research will be performed under the direction of EPA's Air and Energy Engineering Research Laboratory. EPA will use the expertise of Dr. Howard Greene at the University of Akron to conduct the research. These efforts will be coordinated with Capt. Edward Marchant of the USAF.

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## **SERDP Thrust Area: Compliance**

### **Title: Atmospheric Chemistry of Model Air Force Pollutant Compounds**

#### **Problem Statement:**

The goal of this project is to characterize a generalized series of mechanisms by which organic pollutants released during Air Force operations or accidents react during solar irradiation in the atmosphere.

The Air Force uses large quantities of volatile organic liquids as fuels and fire extinguishing agents, and during manufacturing and maintenance operations. Most of these materials qualify as volatile organic compounds (VOCs), because they contribute to photochemical formation of smog and ozone. However, the extent to which each contributes to these processes depends on its respective photochemistry. In conjunction with dispersion models, computational models of reactivity as a function of structure will be a valuable tool for identifying quantities of these organics that can be released without exceeding ambient air quality standards. This effort will contribute to the base of reaction information from which such models of atmospheric reactivity will be generated.

This is a new project which will measure rate constants and products formed from strained hydrocarbon fuels and fluorinated fire extinguishing agents.

#### **Project Description:**

The technical objective of this project is to quantify rate constants for the principal (direct and indirect) photochemical reaction pathways followed by a representative set of examples of strained hydrocarbons and of fluorocarbons and bromofluorocarbons.

The technical approach is to expose dilute gaseous solutions of the respective organic species in simulated airs of varying composition to artificial light at selected frequencies from the solar spectrum. These reactions will be conducted in any of several existing atmospheric chambers, which are specialized to support analysis of the course of the reaction or of the products by gas chromatography coupled with mass spectrometry or with infrared spectroscopy (IR), or by long-path Fourier-transform IR.

This project fits in section 2.A.2 of Tri-Service Environmental Quality Strategic Plan as part of Atmospheric Chemistry of Pollutants.

Elucidation of the atmospheric fate of Air Force chemicals has been a major component through several reorganizations of the Environmental Quality Laboratory. This effort builds on methods developed and verified for simpler structures, and it will expand the base of quantitative information about atmospheric reactions of organic molecules.

The major tasks in accomplishing the goals of this project are to measure the rate constants for disappearance of original organic, measure rates of appearance of products, and to identify and measure rates of formation and disappearance of intermediated products.

This effort will supplement knowledge gained from previous research conducted in AF laboratories investigating the atmospheric chemistry of VOCs.

The technical risks of this project are minimal--the experimental technology is well-developed, and the two classes of compounds selected for study are readily available and stable to conditions of purification.

**Expected Payoff:**

Air Force (and other DoD and civilian agencies) will be able to decrease the risk of implementing another Halon 1211 or CFC-113, with the attendant costs of remediation and disposal of the material and development and qualification of a replacement. For compounds exhibiting acceptable levels of atmospheric reactivity, the models will allow cost-effective tuning of control technologies to provide compliance with air quality standards.

**Milestones:**

Lab facilities in place	Apr 93
Study OH Chemistry and Kinetics	Sep 93
Examine Combustion Properties	Mar 94
Study Ozone Chemistry and Kinetics	Jan 95
Study NO <sub>2</sub> and NO Chemistry and Kinetics	Sep 95

**Transition Plan:**

Reaction schemes and rate constants will be incorporated into Air Force Photochemical Model Upgrade, scheduled as an FY96 start under thrust 2.A.2. Sequential refinements of the photochemical model will be distributed at appropriate stages of that program, and presumably continue to be improved by validation testing and as additional data on new compounds become available. The Air Force Center for Environmental Excellence's Technology Transition Division will be continually advised of the status of this research and will assist in the transition throughout the Air Force, to other federal agencies, and to the private sector.

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
255	185

**Technical Point of Contact:**

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## **SERDP Thrust Area: Compliance**

**Title:** Encapsulation of Hazardous Ions in Smectite Clays

### **Problem Statement:**

This basic initiative seeks to develop new and novel materials for the long term storage of hazardous metal ions, particularly those of toxic heavy metals and radionuclides. The approach to be used is based on fundamental work on chemically stable organic monolayers at Harvard University and the Weizmann Institute. It involves the long-term encapsulation of ions in a new class of hydrophobic smectite clays, whose properties can be tailored to the specific chemical requirements of a particular hazardous species. The key idea behind this experimental program is the initial introduction of hazardous cations into the matrix of clay minerals, followed by the encapsulation of the system with hydrophobic agents. Other variations on this theme will also be pursued, including the direct synthesis of hydrophobic clays around a hazardous cation.

Recent research in several laboratories has focused on the use of clays for environmental remediation. Because of the inherently low cost of natural clays and their ubiquitous presence in nature, the Department of Energy has called for additional research in this promising area. Current investigations have sought to develop ways to utilize these materials for the solution of problems in both organic and inorganic environmental contamination. This proposal seeks to combine the results of previous studies with our own expertise in surface modification of inorganic and polymeric substrates to create a new class of materials for use in environmental restoration.

Smectite clays consist of sheets of aluminosilicates which are separated by an interlayer which contains both inorganic cations, such as calcium and potassium, and water molecules. The cations in native clays can be easily replaced by other cations through aqueous ion-exchange processes. Therefore native clays can be readily used as filters for the removal of hazardous heavy metals and radionuclides. For the remediation of organic materials, clays are traditionally treated with quaternary ammonium cations that contain one long chain hydrocarbon tail. These cations render the surface of the clay hydrophobic. The resulting materials have a greater affinity for non-polar and modestly polar organic compounds.

In the traditional approach for creating hydrophobic clay surfaces, the inorganic cations of the clay are replaced with quaternary organoammonium equivalents. This method is, however, inappropriate for hydrophobic encapsulation of hazardous ions. Creation of a hydrophobic clay by this process after a hazardous metal ion has been exchanged into the interlayer will only cause the release of the harmful species back into the environment. Clays which simultaneously bind hazardous cations and are hydrophobic are, however, of great interest. Such clays should exhibit an increased resistance to leaching of the hazardous ions out of the interlayer by water. These clays would therefore require less stringent storage conditions once a hazardous material had been placed within them. Alternative methods, ones which do not rely on ion-exchange, are required to create these desired hydrophobic clays. The development of these methods, and the characterization and testing of the materials which result from them, is the subject of this proposal.

### Project Description:

The research described in this proposal seeks to replace the traditional cationic methods for creating hydrophobic clays with alternative general approaches which do not require the use of charged hydrophobic species. Specifically, we shall covalently bind alkylsilane groups ( $\text{CH}_3(\text{CH}_2)_n\text{Si}-$ ) to the surface of the clay. This approach therefore will satisfy two simultaneous objectives. First, it will maximize the capacity of the clay for the cation of interest. Since clays are electrically neutral, there is a maximum limit to the number of cations which can reside in the interlayer. By covalently binding the hydrophobic species to the surface, all of the cationic charge within the clay's interlayer is reserved for the cation whose encapsulation is desired. Consequently, the volume required by the storage medium for a given amount of hazardous waste will be minimized.

In contrast, the use of quaternary ammonium salts to change the surface properties of a clay requires that some of the charge capacity within the interlayer be reserved for the hydrophobic species. Second, the use of covalent bond to attach the hydrophobic medium to the clay eliminates the possibility that the modified clay can revert by ionic exchange back to the hydrophilic state. For example, the quaternary ammonium salts could exchange with protons in the environment, thus eliminating the hydrophobicity of the clay. With the organic species removed, the hazardous materials within the clay are susceptible to extraction by water and the ions contained within the fluid. The covalent link between an alkyl chain and the surface of a clay, which is the basis of this proposal, is much more stable to the environment.

The resultant silicon-oxygen bonds are stable to strong acids, water, and organic solvents. Although this bond is susceptible to strong base, it resists attack under common environmental conditions. Previous work has demonstrated that dense monolayers containing from 2 to 18 atoms per alkyl chain form on surfaces of amorphous silicon oxide. Since clay minerals also possess surface  $-\text{OH}$  groups, the techniques developed for the creation of monolayers on silica should also be applicable to these aluminosilicates.

In addition to their reaction with surface  $-\text{OH}$  groups, the silanes react with surface water molecules, thereby forming silicon-oxygen bonds between adjacent alkylsilanes. The network of siloxane ( $-\text{Si}-\text{O}-\text{Si}-$ ) bonds which is formed by this process constitutes a stable cross-linked structure that is held in place by bonds to the substrate and to adjacent silanes. This structure is of higher molecular density than that which can be achieved within clays through the use of alkylammonium cations. Since the latter possess an electrical charge, their density within the clay is limited by the charge capacity of the clay. For example, other workers have demonstrated that neutral organic species can intercalate into hydrophobic clays created by treatment with quaternary ammonium salts. In contrast well-formed monolayers of alkylsilanes prevent the penetration of even organic species into their structure. Therefore, this type of monolayer is expected to be an even more effective barrier to the entry of both polar and non-polar solvents into the interlayer of a clay that contains a hazardous cation. This fact is a further motivation for pursuing covalently modified clay surfaces.

The presence of the cations in the interlayer of a clay represents a possible complication for the formation of the alkylsilane structures. The characterization of the cation in the

hydrophobic medium will therefore be a major part of this project. In most cases, the positively charged species in a clay's interlayer are surrounded by solvating water molecules. It is quite probable that, during the encapsulation process, these water molecules will also react with the alkylsilanes. Such a process would further entrap the cation within the hydrophobic structure.

The nature of this project requires a multidisciplinary approach to the creation, characterization, and testing of this new class of clays. The initial focus of the research will be the determination of the best experimental conditions for the creation of the hydrophobic clays. One crucial question to be answered is whether solution or vapor phase depositions for the silanes are better for this problem. The traditional techniques for the creation of silane monolayers have relied on the use of solutions of the silane in organic solvents. However, using gaseous silanes may enable the silane to penetrate further into the interlayer of the clay and form a more extended network of silanes. The greater size of the hydrophobic barrier which results from vapor phase depositions may result in a structure which is even more stable to the environment.

Once the clays have been modified, they will be evaluated to determine how successfully the newly created barriers prevent the migration of the hazardous cations out of the interlayer. For these studies environmental stresses, both chemical and physical, will be simulated. Several analytical techniques, including X-ray powder diffraction and atomic absorption and UV-visible spectroscopies, will be used to characterize the stability of the hydrophobic layer and the changes which the clay itself undergoes during the simulations. The results of these measurements will characterize how the clays withstand various stresses and how much material leaves the clay and enters surrounding fluids.

#### **Expected Payoff:**

The new clay materials created during this study offer the possibility of improved long term storage for metallic cations whose re-entrance into the environment is undesirable. For dilute radioactive wastes, clays can be used to filter the waste species out of the ambient medium. The resultant radioactive clay minerals unfortunately pose several problems for long term storage. If exposed to polar solvents that contain other cations, the immobilized radionuclei can re-exchange out into the fluid. Rendering these clays hydrophobic without resorting to charged surfactants such as quaternary ammonium species will result in materials that are much more resistant to typical environmental stresses. Therefore less rigorous isolation methods will be required for long term storage of these hazardous materials.

The modified clays will have a much different affinity for water than unmodified clays and other minerals. This difference should provide an effective means for separation of the hydrophobic materials from native minerals. If the hydrophobic clays are accidentally remixed with other minerals, re-separation should be simple because of the drastically different flotation properties of the former.

The raw materials for this project are inexpensive. Clays are a major constituent of the earth and have many industrial uses. They have been proposed for a variety of environmental uses where cost minimization is important consideration, such as in the recovery of fossil

materials from the environment. Organosilanes have been used for over three decades for the creation of reverse-phased chromatographic column packings. They are also extremely inexpensive and readily available. Thus novel chemical concepts will be coupled in a rational way to provide a practical solution to a significant environmental problem.

#### **Milestones:**

##### **First Year:**

Native clays will be used to examine both solution and vapor-phase creation of barrier layers on the surface of the clay. The properties of clays which are treated with a series of silanes that differ in the number of carbon atoms in the alkyl tail will be compared. In addition, hydrophobic clays will also be prepared by the traditional method of cation exchange. The latter substance will provide a useful comparison for the efficacy of the silylated systems.

In the past, alkylsilane monolayers have been created from alkyltrichorosilyl species. However, dialkyl or trialkyl species may offer significantly improved surface properties. While many of the monoalkyl species are available commercially, some of the di- or trialkyl species may have to be synthesized.

##### **Characterization:**

The first stage of this project will be to thoroughly characterize the native and ion-exchanged clays. Power diffraction will be used to determine the spacing between the sheets of smectite clays. The surface area of the clays will also be determined by BET isothermal measurements. Similar measurements will be performed on clays into which transition d- and f-elements have been introduced. The database created by these measurements will permit the discrimination of those effects which arise from exchange of the cation within the clay and those which are due to the presence of the hydrophobic surface layer.

##### **Testing:**

Most of the testing of the hydrophobic clays will occur during the second and third years of this project. At the end of the first year, however, some of the evaluation procedures discussed below will be initiated.

##### **Second Year:**

The primary focus of the second year will be in evaluating the effectiveness of hydrophobic clays in encapsulating hazardous ions. For these studies the substrate will now consist of ion-exchanged clays which contain transitional metal ions. These clays will be subjected to the hydrophobic treatment which was optimized during the first year.

##### **Characterization:**

The modified materials will be analyzed using the techniques discussed above. In addition, X-ray absorption spectroscopy will quantify the changes, if any, in the local (<5 angstrom)

environment experienced by the cation when the clay is exposed to both polar and non-polar solvents. We will also use anomalous small angle X-ray scattering (ASAXS) to examine the distribution of exchanged cations within the interlayer of the clays.

#### Testing:

The evaluation of the hydrophobic clays requires the monitoring of the composition of the solvents to which the clays are exposed over a period of time. These studies will begin during the second year. Immersion of the modified clays in various solvents for extended periods will simulate the effects of such solvents in nature. The composition of the surrounding solvent will be quantified, thereby indicating how effectively the modified clays retain their cations. Hydrophilic clays will undergo the same simulations, thus functioning as a control for the characterization of the hydrophobic materials. These tests will continue into the third year.

#### Third Year:

During the first two years of this project we will focus on natural clay minerals. During the third year we will examine alternative methods for encapsulating ions into clay minerals via in situ synthesis of the clay. The Argonne Chemistry Division has an on-going program in synthetic clays. The methods developed by this program will be applied to solutions which contain representative transition d- and f- cations. These experiments will attempt to achieve quantitative immobilization of the model cations within a clay lattice and interlayer.

#### Characterization:

The synthetic clays will be evaluated by a variety of methods. Powder diffraction and surface area measurements will provide one indication in the success of the synthesis of the clays. Small angle neutron scattering will be used to determine to what degree a layered structure has formed in the synthetic material. The reactant solution will also be analyzed for its elemental composition, thus indicating how effectively the cations of interest have partitioned between the reactive medium and the synthetic clay.

#### Testing:

The long-term testing programs initiated during the second year will be continued. The protocols will also be applied to the new synthetic materials.

#### Transition Plan:

This project relies on the cooperation of several research groups. The principal investigators are members of the catalyst and clay programs at Argonne National Laboratory. The personnel and the facilities of the Chemical Separations Science and Heavy Elements Coordination Chemistry groups of the Argonne Chemistry Division will help in the preparation and characterization of clays with tracers and other radioactive constituents. Scientists at the American Colloid Company of Arlington Heights, IL, a supplier of clay minerals for a variety of industrial uses, have agreed to consult on the creation and use of hydrophobic clays.

**Funding:**

This proposal will require the services of one full-time staff member and one post-doctoral appointee for the duration of the project.

The following table summarizes the costs for manpower, materials, supplied, analytical services, and overhead.

	Year 1	Year 2	Year 3	Total
Effort				
Scientific Staff- months	24	24	24	72
Technical Services - months	6	6	6	18
Total Months	30	30	30	90
Total Effort in Years	2.5	2.5	2.5	7.5

	Estimated Cost (in Thousands)	
	FY93	FY94
Effort	\$216	\$229
Material and Services	\$48	\$50
Overhead and Assessments	\$88	\$92
Capital Equipment	\$0	\$0
Total Estimated Cost	\$352	\$371

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## **SERDP THRUST AREA: Compliance**

### **Title: Fundamental Studies of Hazardous Metal-Ion Separations Chemistry**

#### **Problem Statement:**

This project will (1) enhance fundamental understanding of the coordination chemistry of hazardous-metal-ion complexation and (2) exploit this knowledge to develop improved separations for analytical methods, metals processing, and waste treatment.

Actinides and hazardous radionuclides (RA, Pu, AM, U, Cs, Sr, etc.), and other toxic metals ions (Pb, Hg, Cr, Cd, etc.) must be removed or recovered from the environment (e.g., contaminated soils, sludges; mine ores; process wastes; and geothermal and gas and oil well waters) at a variety of DOE and DoD sites (e.g., Hanford waste tanks, Hg and Pb spills at LANL and ORNL, etc). United States industry produces a variety of waste streams including waste catalysts, electroplating waste waters, electronic wastes, and oil drilling and geothermal wastes waters. These waste streams would greatly benefit from research and development of metal-ion separations.

Because general metal-ion separations is such a broad area, this proposal is initially focused on specific hazardous metal ions and specific challenges presented in both classical liquid-liquid biphasic extraction and the newer separations arena of water-soluble chelating polymers. Quite different aspects in separations are being addressed, so this proposal has been divided into subtasks each with its own research objective, scientific background, and approach with the accompanying funding and activities.

#### **Subtask 1: Fundamental Toxic-Metal-Ion Separations Chemistry of Water-Soluble Chelating Polymers**

This subtask will investigate features of water-soluble chelating polymers that effect their binding constants and selectivity for selected metal ions.

The use of water-soluble chelating polymers with ultrafiltration is a relatively new approach for metal-ions separations. Bayer has best demonstrated the technique in the 1980s for transition metal-ion separations and has performed some work with actinide binding using 8-hydroxyquinoline attached to polyethyleneimine. The use of water-soluble chelating polymers has been extended to a variety of application using a broader range of chelators, some under development at LANL.

Characterization of the polymers upon functionalization with a chelating group can be difficult, as it is in most polymer systems. Water-soluble polymers do have an advantage because solution-based analysis techniques (e.g., NMR, UV, titration, etc) can be used for their evaluation. Several questions must be answered: (1) What effect does the linking group have on metal-ion binding of the ligand and is it greatly different from the free ligand? (2) What is the density of the chelate group? (3) What is the effect of the polymer size and type on selectivity and binding constants of the attached chelator? (4) Do the ligands function similarly in an aqueous-based system and an organic-aqueous, biphasic extraction system? (5) Do the functionalized polymers interact with the ultrafiltration membrane surfaces in a

different way from the free polymer?

#### **Project Description:**

This proposal will be using a multipronged approach. Examples of studies include (1) Studying C-13 labeling to determine the extent of functionalization using NMR; (2) synthesizing different linking groups and determining their effect on metal-ion binding; (3) determining protonation constants potentiometrically and correlating them with specific sites on the ligand using variable pH/NMR studies; (4) evaluating the ligands potentiometrically in the presence of the metal ion of interest and determining the binding constants; (5) correlating of complex equilibria with potentiometric data using spectroscopic techniques (NIR, UV-Vis); (6) studying metal-ion selectivity on selected systems.

A program at LANL exists in ligand design for metal-ion separations, in which ligands or complexants are developed and then chemically bound to water-soluble polymers for development of applications to metal-ion separations. The applications include "Recovery of Toxic Metal-Ions from Electroplating Baths" (joint with Boeing Aerospace), "Development of Ultralow Analysis of Actinides" (Mixed Waste Integrated Demonstration), and "Waste Water Treatment for Actinide Removal" (Efficient Separations and Processing Integrated Program). There is leverage with these projects, but none of the applied projects have built-in a basic research component that allows for enhancing our fundamental understanding of these systems.

#### **Task/Milestone/Funding Summary:**

- a) synthesis of selected chelating polymer (FY93) (\$200K)
- b) labeling experiments (FY93) (\$200K)
- c) solution characterization studies (FY94) (\$126K)
- d) spectroscopic studies (FY94) (\$100K)
- e) potentiometric studies (FY95) (\$150K)
- f) integration and transfer of technology as appropriate to next phase (FY95) (\$150K)
- g) annual reports (deliverables) (one each in FY 93, 94, 95)

#### **Subtask 2: Radium-, Cesium- and Strontium-Selective Complexing Agents**

This subtask will focus on the design, synthesis, and characterization of macrocyclic polyether ligands that are capable of selectively complexing radium, cesium, and strontium from a variety of aqueous media (basic or acidic).

Efforts to devise new complexants for radium (cesium and strontium) are complicated by the low charge density of the  $Ra^{+2}$  ion. To date, development work on  $Ra^{+2}$  complexation has focused on inorganic sorbents, i.e., manganese oxides, and on macrocyclic polyethers, i.e., dicyclohexano-21-crown-7. None of these systems has proved satisfactory for the development of  $Ra^{+2}$ -specific extractants, resins, or polymeric sequestering agents.

Recent advances in computer-assisted molecular design and macrocyclic polyethers chemistry, however, have increased the likelihood that  $Ra$  specific ligands can be developed.

**Project Description:**

This subtask calls for use of the CAChe (Computer-Assisted Chemistry) modeling system to design macrocyclic polyethers in which the host molecule (i.e., the crown ether) is highly preorganized for binding or complexation to a  $Ra^{+2}$ , or similar ions (i.e.,  $Cs^{+1}$ ,  $Sr^{+2}$ ). The more highly the macrocycle is preorganized for binding, the more stable the complex. Using modeling programs should allow us to vary steric and electronic modifications on the ligand and determine their effect on the stability of the complex without having an initial major effort in organic synthesis.

After the design stage, the most promising coplexants will be synthesized and evaluated. Radiochemical techniques will be used to measure the stability of the complexes and biphasic partitioning techniques will be employed to evaluate the selectivity of the reagent for radium, alkali, alkaline earth, iron (II and III), and aluminum.

**Task/Milestone/Funding Summary:**

- a) computer modeling phase using CAChe on three model unsubstituted crown ethers (FY93) (\$60K).
- b) computer iteration of varying ring-size, substituent effects, donor atoms, etc. (FY93) (\$65K)
- c) synthesis and characterization of best candidates from modeling studies (FY94) (\$65K)
- d) Ra complexation studies/biphasic partitioning (FY95) (\$125K)
- e) annual reports (deliverables) (one each in FY93, 94, 95)

**Subtask 3: Determination of the Role of Organic Solvent in Selective Alkali and Alkaline Earth Extraction**

This subtask will determine the role of the organic solvent in selective alkali and alkaline earth using cesium and strontium as example metal ions.

Efforts to improve available methods for extracting several of the alkali and alkaline earth elements are complicated by their low charge density and the resultant unfavorable thermodynamics for transfer of their complexes from aqueous environments into typical organic solvents. Comparatively little attention has been devoted to examining the role of the organic solvent in governing the effectiveness of a particular extractant for the elements. It was recently determined that certain aliphatic, oxygenated solvents are capable of accommodation hydrated anions. This capability has been utilized to enhance strontium extraction from nitric acid-containing media by certain crown ethers. A potentially fruitful approach to enhancing the extraction of strontium and cesium from basic media is to combine an appropriate crown ether with a solvent that is capable of dissolving substantial quantity of water. An improved understanding of the basic chemistry of such solvent systems is required to more fully exploit this effect, in particular to extend it to ions other than strontium and to strongly alkaline media.

**Project Description:**

This subtask will focus on the organic solvent aspect of extraction systems employing

macrocyclic polyether ligands developed in subtask 2 or similar models. The relationship between the water content of a solvent and the efficiency of metal-ion extraction and various solvents and extraction characteristics, and of mixed solvent systems will all be examined.

**Task/Milestone/Funding Summary:**

- a) correlation of metal-ion extraction with solvent water content for single-solvent systems (FY93) (\$50K)
- b) determination of solvent molecular weight, branching, functional group, etc. effects (FY93) (\$70K)
- c) determination of aqueous phase parameters such as temperature, basicity, ionic strength, etc. (FY94) (\$70K)
- d) optimization of extractant structure in high-water-content solvents (FY94)
- e) studies of mixed solvent extraction (FY95) (\$67K)
- f) determination of factors governing the solubility of polar molecules in nonpolar solvents (FY95) (\$125K)
- g) annual reports (deliverables) (one each in FY93, 94, 95)

**Expected Payoff:**

The fundamental knowledge obtained from these studies should advance the state of metal-ion separations to allow for application to a variety of real-world environmental problems, for example, removal of lead and mercury from soils, tank waste treatment at Hanford, decontamination and decommissioning of DOE facilities, controlling the NORMs (naturally occurring radioactive materials) at geothermal and oil drilling sites, and general site characterization.

**Funding: (\$K)**

FY93	FY94
450	500

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## **SERDP Thrust Area: Compliance**

**Title:** Dispersion in the Convective Boundary Layer

### **Problem Statement:**

The objective of this program is to provide fundamental understanding of diffusion phenomena in the convective boundary layer, such as plume penetration of elevated inversions, top-down versus bottom-up diffusion, nonhomogeneous and nonstationary surface heating, and concentration fluctuations.

Much of our current knowledge of dispersion in the convective boundary layer (CBL) is due to the laboratory convection-tank simulations by Willis and Deardorff. Their simulations have enhanced our understanding of 1) the mean concentration fields resulting from releases of passive material from various heights within and above the CBL, 2) the mean fields resulting from releases of buoyant effluents, and 3) the fluctuating concentration fields for either passive or buoyant releases from a single release height. These studies have also provided stimulus, guidance, and data for the development of improved dispersion models. New models for the mean concentration fields based on these laboratory simulations show much better agreement with field observations than do the older Gaussian-plume models, and this is especially true for buoyant releases from tall stacks.

While much progress has been made from these simulations, there are a number of extensions that would enhance our understanding and improve our predictive capability. This is especially true for concentration fluctuations. Such concentration fluctuations are probably greatest during convective conditions, and knowledge of them is important in evaluating the performance of the mean concentration models, in estimating the exceedance of air-quality standards, and in predicting the toxicity or flammability limits of hazardous substances.

An initial effort on top-down versus bottom-up diffusion is currently being funded with SERDP Phase 1 monies.

### **Project Description:**

This study would examine the dispersive properties of the convective atmospheric boundary layer through laboratory simulations in the EPA convection tank, and would include effects of plume penetration of elevated inversions, top-down versus bottom-up diffusion, and non-homogeneous and nonstationary surface heating and, particularly, concentration fluctuations. Parameters to be varied would include surface temperatures and heating rates, ambient stratification, inversion heights, release locations, and types of nonuniformities in surface heating. Quantitative measurements would be made of the developing flow and concentration fields to be used in the development and evaluation of convective diffusion models.

NCAR and DoD have funded extensive field studies and large-eddy-simulation modeling efforts to collect data on the convective boundary layer. Both organizations are very much interested in the continuation of the laboratory convection-tank simulations.

**Expected Payoff:**

Improved environmental management and compliance with air-quality standards --  
Development and evaluation of models to predict exposures to pollutants released during  
daytime convective conditions in the atmospheric boundary layer.

**Milestones:**

Data Report on Top-down vs. Bottom-up Diffusion	FY93
Journal Article on Top-down vs. Bottom-up Diffusion	FY94
Data Report on Plume Penetration of Elevated Inversions	FY94
Journal Article on Plume Penetration of Elevated Inversions	FY95
Data Report on Non-homogeneous Surface Heating	FY95
Journal Article on Non-homogeneous Surface Heating	FY96
Data Report on Statistics of Concentration Fluctuations	FY96
Journal Article on Statistics of Concentration Fluctuations	FY97
Final Report	FY97

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
200	200

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## **SERDP Thrust Area: Compliance**

**Title:** Fundamental Studies of Thermal, Plasma, and Photochemical Processing for Waste Disposal Applications

### **Problem Statement:**

The objective is to develop fundamental knowledge of high temperature thermal, plasma, and photochemical processes as applied to Army waste destruction. Particular focus will be on studying the effect of photochemical action on incineration-type flames especially as applied to the destruction of hazardous compounds containing halogens, phosphorus, and sulphur, and on non-thermal and thermal plasma research as applied to solid, liquid, and gas pollutant processing. It is expected that flame photochemical action and novel plasma approaches, when coupled with high temperature incineration, will result in superior performance with respect to the completeness of hazardous material destruction and minimization of pollutant gas generation.

The Army generates vast quantities of waste each year. A certain amount of that waste, such as that generated during P&E production, is unique to the Army/DoD and represents a major challenge with respect to proper disposal in an environmentally acceptable way. Incineration is a current method of waste disposal which is only partially successful in hazardous waste disposal. Problems still exist with respect to complete destruction of the hazardous compounds, creation of new hazardous compounds and pollutants in high temperature flames (such as dioxins), as well as the production of residuals (ash) that need to be disposed of further. The photochemical incineration and plasma technologies show considerable promise for improved destruction of hazardous wastes with minimal production of pollutant gases.

### **Project Description:**

This project will utilize the combustion and plasma diagnostics capabilities located at the ARL. Incinerator simulation flames will be studied using molecular beam/mass spectrometric (MB/MS) sampling as well as laser diagnostics and the effect of photochemical action on hazardous compounds will be determined. Flame photochemical action on hazardous compounds which contain halogens (such as PCP), phosphorus (chemical agents), and sulphur is expected to lead to improved destruction efficiency and cleaner exhaust gases. Similarly, plasma technologies will be studied with respect to their potential for improved destruction of waste compounds. Thermal plasmas offer superior destruction potential over incineration due to their much higher energy environment which leads to a higher degree of destruction of the original hazardous compound. However, thermal plasmas generate gaseous waste streams heavily laden with the oxides of nitrogen. Non-thermal plasmas, on the other hand, have recently been shown to be very effective in de-NO<sub>x</sub> and de-SO<sub>x</sub> applications. However, the specific physical and chemical processes that result in the reduction of the pollution gas stream are not well understood. Thus, there is a considerable amount of fundamental research to be done concerning the specific plasma approaches, such as plasma arc, pulsed coronas, glow discharge, microwave, etc. In our proposed research, plasma waste processing simulators will be developed and studied and the optimal plasma approach will be identified.

### Expected Payoff:

Significant improvements in our understanding of high temperature thermal, photochemical, and plasma processes as applied to waste destruction has a wide range of potential benefits to many Army operations. These include the destruction of volatile organic compounds (VOCs) from various Army installation and depot operations, improved destruction of chemical agent stockpiles, as well as the destruction of large stockpiles of pentachlorophenol (PCP) treated ammunition boxes by incineration. The problem in the latter case is the concern over dioxin formation during regular/unassisted incineration.

### Milestones:

There has been relatively little work done on the fundamental understanding of the detailed chemical processes involved in incineration flames. There has been virtually no work done in the use of photochemistry as a destruction augmentation means in high temperature incineration. However, recent advances in high intensity excimer lamp technology makes the practical use of uv radiation in incineration applications a realistic possibility. As far as thermal and non-thermal plasmas are concerned, there has been very little fundamental work done with respect to the interaction of the plasmas with typical pollutant gases.

- |   |      |
|---|------|
| -Initiate incinerator simulation flame structure studies to establish base performance.           | FY93 |
| -Develop kinetic and thermochemical data base for hazardous compounds.                            |      |
| -Construct plasma waste processing laboratory simulators.   |      |
| -Study the effect of photochemistry on hazardous compound (e.g. PCP) destruction.                 | FY94 |
| -Develop detailed chemistry flame mechanisms relevant to hazardous compound incineration.         |      |
| -Model photochemically altered flames.  |      |
| -Initiate plasma studies.   |      |
| -Identify and develop specific photochemically-assisted incinerator approach.                     | FY95 |
| -Identify and develop specific plasma waste disposal approach.                                    |      |
| -Develop small-scale photochemical flame incinerator.   | FY96 |
| -Develop small-scale plasma waste processor.  |      |
| -Demonstrate improved performance on laboratory-scale high temperature photochemical incinerator. | FY97 |
| -Demonstrate pollutant stream clean-up using laboratory-scale plasma waste processor.             |      |



**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
In-House	300	325
Contract	50	75
Total	350	400

**Performers:**

This project will be done jointly with Dr. Wing Tsang, National Institute of Standards and Technology (NIST). This project will also be strongly coordinated with CERL, which has an active program on plasma arc destruction of Army wastes.

In addition to the coordinated work with OGAs, there is considerable opportunity for involvement with certain companies in the pollution control industry under a Cooperative Research and Development Agreement (CRDA). Specific companies that would be targeted are ones involved in thermal and non-thermal plasma pollution control technologies.

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## **SERDP Thrust Area: Compliance**

**Title:** Energy Conservation and Air Toxic Compliance Plan for DoD Industrial Facilities

### **Problem Statement:**

Defense Energy Program Policy Memorandum (DEPPM) 91-2 and Executive Order 11752 assign energy efficiency goals for Federal facilities for Fiscal Year (FY) 2000 as compared to an FY 1985 base year. In particular, each DoD component is directed to prescribe policies and establish appropriate measures of energy efficiency under which the aggregate of its industrial energy-consuming facilities will increase energy efficiency by at least 20 percent in FY 2000 in comparison to FY 1985.

Title III of the Clean Air Act Amendments of 1990 directs the USEPA to establish criteria controlling the emissions of 189 air toxic chemicals. The majority of these air toxic emissions come from industrial activities. Regulations governing the control of emissions of these chemicals from industrial activities are being developed by USEPA beginning in 1992 for 41 source categories, and continuing through 2000 for the remaining 250 source categories.

The vast majority of DoD industrial activities utilize technologies that are over 40 years old. These new energy and environmental directives in most instances exceed the performance capabilities of DoD's installed industrial technologies. Future DoD industrial facilities will employ state-of-the-art production technologies being developed jointly by the Army's ManTech program and DOE's Sandia National Laboratory. The problems occur in the existing DoD industrial base where cost effective compliance with these directives will require a thorough evaluation of DoD industrial activities and their potential for improvements.

### **Project Description:**

The objective of this new research project is to develop a strategy by which the DEPPM industrial energy efficiency goals and Clean Air Act air toxic emissions reduction goals are met in a cost effective manner. This project will identify technologies for the existing DoD industrial base that both reduce energy consumption and reduce air toxic emissions by improving the performance and operation of industrial processes. This project will build upon the following ongoing research programs:

1. Modernization of energy production facilities by the Army, Air Force and EPRI,
2. Air pollutant emission source inventory surveys by the Army and Navy,
3. Industrial energy auditing surveys being conducted by the Army,
4. Air toxic emissions source survey developed by Navy and Air Force for the Navy facilities in San Diego, CA, and
5. Industrial air toxic emissions research being conducted by the USEPA's Air and Energy Engineering Research Laboratory.

The project will attempt to extend the mass and energy flow modelling concepts being used in these research projects to industrial activities and their potential air toxic emissions. This research effort will develop a coordinated compliance strategy for DoD industrial facilities by

accomplishing the following tasks:

TASK I -- Develop, in coordination with DoD energy management proponents and DoD industrial facilities representatives, a workable definition of industrial energy consuming activities. For each DoD industrial activity, determine quantifiable output parameters for both active and inactive processes.

TASK II -- Define, in coordination with USEPA, DoD industrial activities likely to fall under air toxic emissions regulations, and identify potentially regulated air toxic chemicals. Determine the proposed schedule for USEPA regulations, and identify probable emissions control requirements.

TASK III -- Determine the types and relative amounts of DoD industrial energy end use (e.g., machining, heat treatment, chemical processing, etc.). Review current private sector industrial energy management procedures and air toxic compliance strategies to determine the potential for energy efficiency improvement and air toxic emission reduction in each of the various end use categories. Based on the proposed regulatory schedule, develop energy and material flow models for DoD industrial activities. Use these models to identify opportunities for making improvements to operating and maintenance procedures, and applying new technologies which both reduce energy consumption and reduce air toxic emissions.

TASK IV -- For those industrial processes that must be completely re-engineered to remove air toxic emissions, evaluate the new production technologies being developed by the Army ManTech program and DOE to define their air toxic emission potentials. Examine the missions and current production levels for each DoD industrial facility to determine the feasibility of consolidation of facilities to allow some facilities to be closed or placed in stand-by status. Examine the feasibility of mission realignment among active facilities to decrease the number of active industrial facilities that must be re-engineered.

TASK V -- Develop a prioritized implementation plan to bring DoD industrial activities into compliance with energy efficiency and air toxic emission reduction goals in a cost effective manner.

#### **Expected Payoff:**

The Army was having difficulty in attaining the required 1985 energy reduction goals for industrial facilities of 8 percent by 1995. Currently less than 1/3 of the Army's industrial facilities are on target to meet their energy reduction goals. Now that the goal has been increased to 20 percent by 2000, Army industrial facilities will have to adopt a more accelerated energy reduction program. Beginning in 1995, the Clean Air Act Amendments will require DoD industrial facilities to significantly reduce their overall emissions of air toxic chemicals. This research will produce a prioritized implementation plan that will effect over 75 industrial facilities in DoD.

**Milestones:**

Identify significant industrial energy uses	FY93
Identify significant air toxic sources	FY94
Develop industrial process models	FY95
Define conservation/control opportunities	FY96
Evaluate new industrial process air toxics	FY96
Develop coordinated implementation plan	FY97

**Transition Plan:**

Because the users of this research project will be a critical part of the research team, the transition of this project's proposed implementation plan into action is expected to be smooth. The results of this study will form the basis for modernization plans for industrial facilities, as well as, remediation plans for cleaning up air toxic emission sources.

**Funding: (\$K)**

	FY93	FY94
OCE	0	95
AMC	200	
SERDP	550	550

**Performers:**

The primary performing agency will be the US Army Construction Engineering Research Laboratories with extensive support from the US Army Toxic and Hazardous Materials Agency and the Production Base Modernization Program of the US Army Munitions Command. Additionally, the extensive experience of USEPA's Office of Air Quality Planning & Standards, USEPA's Air and Energy Engineering Research Laboratory, and DOE's Sandia National Laboratory will be used. Other laboratories and private research organizations (e.g., EPRI, GRI) will be employed for specific energy saving technologies, air toxic emission control techniques, air toxic emissions monitoring, energy monitoring, and toxic materials modelling. USEPA, DOE, DoD contractors who have demonstrated expertise in environmental and energy auditing, applying energy-conserving and air toxic controls technologies, and developing coordinated management strategies for industrial facilities will also be employed as part of this study.

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**SERDP Thrust Area: Compliance**

**Title: Supercritical Water Oxidation Technology Demonstration**

**Problem Statement:**

The goal of this project is to accelerate the technology transfer of supercritical water oxidation through a joint DoD/DOE field demonstration.

Supercritical water oxidation (SCWO) technology can be used by Navy, Army, and Air Force installations and the DOE complex.

The DoD and the DOE generate large volumes of liquid hazardous wastes as a result of industrial activities such as aircraft and ship rework, vehicle and artillery repair, and weapons production. These wastes include organic compounds such as chlorinated solvents; cutting, hydraulic, and lubricating oils, painting and stripping wastes; organic acids; and radioactive mixed waste. At the present time, these waste are usually disposed by burial in a hazardous waste landfill. The economic and social costs of this disposal method have risen rapidly in recent years. For example, the Navy now spends about \$40M per year to dispose of hazardous organic wastes and still retains legal liability for these materials. A preferred method of disposal is to destroy these wastes and convert them into environmentally benign compounds such as water and carbon dioxide. High temperature incineration is one method of accomplishing this conversion. However, hazardous waste incinerators have become virtually impossible to site and permit.

A possible alternative to high temperature incineration is low temperature oxidation using a process called supercritical water oxidation (SCWO). SCWO technology brings together organic waste, water, and oxygen at a temperature and pressure above the critical point of water (374°C, 22.1 MPa). Above this point, water becomes a single phase fluid with a density near that of a liquid and the transport properties of a gas. Above the critical point, water serves as an effective solvent for organic compounds. Gasses, including oxygen, are also completely miscible. In the SCWO process, organics are quickly oxidized to carbon dioxide and water with destruction efficiencies of over 99.99%.

The DOE Office of Technology Development (EM-50) has also identified this technology as a promising process for destruction of its organic and mixed HW. DOE has established a national program with a short term goal of demonstrating the destruction of organic HW and a long term goal for the treatment of mixed waste based on data derived from the work in this proposal. To achieve this objective, EM-50 has designated the Idaho National Engineering Laboratory as the coordinator for all SCWO related activities being conducted by DOE, other Federal agencies, industry and academia to bring a sharp focus to the overall development and implementation of SCWO for DOE hazardous and mixed waste.

This is a proposed new SERDP program.

## **Project Description:**

The primary objective of this proposed joint effort is to demonstrate SCWO technology, at the pilot plant scale, as a method of destroying selected, non-radioactive, organic hazardous wastes generated by DoD and DOE industrial shop operations.

The proposed joint project will consist of three phases: (1) Demonstration using existing pilot plant, Data Acquisition, and Implementation process development (2) Advanced Pilot Plant Design and Demonstration, and (3) Transition Plans.

Phase 1: (1) In this initial phase of the project an existing SCWO pilot plant will be acquired, leased or rented, to quickly begin a demonstration of the technology at a DoD site currently generating hazardous wastes of interest, such as cutting and lubricating oils. This approach will enable determination of the process necessary for siting and operating a SCWO pilot plant at a DoD installation for treatment of actual RCRA wastes. This process includes, but is not limited to, establishing the permitting requirements; addressing regulator, customer, and public concerns; determining personnel requirements and training; facility requirements; and safety procedures. These issues, although not strictly technical, are critical to the successful implementation of this technology at any point in its development. Obtaining these data and experience now, simultaneously with the on-going efforts by other research groups to solve the technological problems, will significantly accelerate the fielding of the next generation of full scale SCWO plants.

(2) Data acquisition will be the second major component during this initial demonstration. Data will be collected on the plants performance, with selected DoD waste streams (vice the waste surrogates used to-date); on reliability and operability, and on plant design problems. This information will provide input for establishing the criteria for the next generation of pilot plant design and demonstration in Phase 2. It is also anticipated that new information will be available by the end of 1994 from other research projects currently underway, which will provide significant technical data and engineering solutions to current problems with the technology. This information will be combined with the data from this demonstration for incorporation in the designs of the next generation plants.

Phase 2 of this proposal will be the design and demonstration of the next generation system. Transition plans will be prepared in Phase 3.

Tasks: The tasks required to accomplish the proposed project are outlined below:

I. Phase 1: Demonstration using existing pilot plant, Data Acquisition, and Implementation process development. Modify all DOE SCWO project management and execution plans.

Conduct the Pilot Plant site selection.

- a. Identify a DoD site with suitable waste stream
- b. Determine facility and public concerns
- c. Determine personnel and training requirements
- d. Determine facility infrastructure requirements
- e. Generate QA/QC & Safety plans

Acquire a 500 GPD pilot plant (lease or rent existing system);

Data Acquisition.

- a. Performance data, i.e., destruction efficiencies, corrosion effects, data for reliability analyses, etc.
- b. Determine HW materials handling requirements
- c. Operability data, i.e., maintenance schedules, personnel support, down time, max. operation time, etc.

Waste Characterization

- Initial focus will be on waste oils and pretreatment requirements

Preliminary Process Design

- Develop preliminary design for next generation plant. Incorporate knowledge from other research as it becomes available. Design to be modular to simplify future modifications.

II. Phase 2: Advanced Pilot Plant Design and Demonstration

Permitting/NEPA

- Process based on lessons learned in Phase I

Detailed Pilot Plant Design

- Incorporate new information expected from other research efforts, especially ARPA projects

Pilot Plant Fabrication

- Contracted to private industry

Site Selection, Preparation, and Plant Installation

- Same requirements and procedures followed as in Phase I

Develop Test Plan

- Use lessons learned from Phase I; Testing, Operation, and Reporting

III. Phase 3: Transition Design Plans and Implementation Process Plan

This project is directly responsive to DoD and DOE environmental objectives, such as the Army and Navy hazardous waste minimization programs (as expressed in OPNAVINST 5090.1 and similar documents) and DOE's Mixed Waste Integrated Demonstration program.

Advanced development work (6.3B) on SCWO was proposed by the Navy for the DoD Environmental Quality Strategic Plan under the COMPLIANCE pillar; Sub-area: Satisfy RCRA Provisions, Treatment, Advanced incineration capability for hazardous waste (2.III.1b). The proposed work also supports the COMPLIANCE pillar of the recently signed Army Environmental Strategy.

This project will provide baseline support for the non-radioactive component in DOE's program to develop viable technologies for treating mixed radioactive waste. The DOE EM-50 has established a national program to ultimately develop SCWO as a viable treatment technology for mixed waste.

The proposed project does not duplicate any current SCWO programs. The Advanced Research Projects Agency initiated work in March, 1992, to design, build, test and evaluate a 1500 gal/day SCWO pilot plant to destroy chemical warfare agents. The Air Force initiated work in August, 1992, to develop a 1200 gal/day SCWO pilot plant to destroy the propellants from the third stage motors of Minuteman ICBMs. This joint DoD/DOE project will not utilize chemical warfare agents, explosives, propellants, pyrotechnic devices, or radioactive materials as test materials.

The DoD has been supporting the Navy's Exploratory Development (6.2 Program) efforts on SCWO through the Office of Naval Technology. This work appears in the Project Reliance documentation. The Exploratory Development phase, which has included the design and fabrication of a 40 gpd bench scale unit, is scheduled to be completed in FY 93. A proposal for an Advanced Technology Demonstration (6.3A Program) has been submitted by the Navy.

DOE has supported the development of SCWO technology in the past through the Office of Industrial Technology Combustion Program. Involvement from the private sector has been a significant part of this program whose participants include MODEC and MODAR. The efforts have included the development of bench scale units with the emphasis on energy recovery. Through this effort, MODAR has completed the fabrication of a pilot scale unit and has initiated testing on it. Los Alamos National Laboratory has conducted significant research into SCWO chemical kinetics, process design and testing of simulated wastes. Sandia National Laboratory has worked extensively modeling of SCWO kinetics, thermodynamics, and transport.

Laboratory work at universities on specific SCWO topics is expected to expand; work on SCWO hardware development at the three commercial developers of this technology in the United States is expected to continue.

SCWO is a new, high risk technology. Several engineering development issues could limit the development and application. These issues include the corrosive nature of chlorine, sulfur, and other elements released by oxidation of the organic portion of the waste in supercritical water. Large amounts of oxygen must also be added to the process stream, further increasing the problems associated with material integrity. The possibility of a detonation within the system always exists when oxygen is added to organic material. Plugging of pipes, reactor vessels, and other components due to the deposition of metal salts and oxides on interior surfaces is also a problem. Waste handling, preparation and blending; process control; and effluent monitoring and treatment may present other technical risks. Economic competitiveness is another issue. The economic performance of an SCWO system will depend on actual capital and operating costs, reliability, the quantity and composition of future waste streams, and other factors that have not been determined.

#### **Expected Payoff:**

It is estimated that a market exists within the DoD industrial community for approximately 27 large capacity SCWO waste processing plants. These plants are estimated to cost \$8M to \$12M each to buy, and about \$1.5 M/yr each to operate. The estimated waste disposal cost using SCWO is \$10 to \$12 per gallon of waste. This can be compared to the \$15 to \$45 per



gallon presently spent to dispose these wastes. Estimated payback period for a large scale SCWO waste processing plant is 5 years. Estimated annual saving with Navy-wide implementation is \$35M per year. Estimate Army and Air Force saving in waste disposal costs are comparable.

#### **Milestones:**

Project accomplishments during FY93: Assuming funds are released in October, 1993, the expected accomplishments for FY94 are listed below.

- The existing DOE SCWO demonstration project management plan will be modified.
- An existing pilot scale SCWO system will be identified and the system leased or rented.
- A DoD site will be selected for this demonstration. Potential DoD sites that have been identified include: the Naval Aviation Depot, Norfolk, VA; the Naval Public Works Center, San Diego, CA; the Naval Surface Warfare Center, Indian Head, MD; the Army Arsenal, Watervliet, NY; and the Army Arsenal, Picatinny, NJ.
- The implementation process will be developed and executed.
- Plant installed and brought on line.

Demonstration will be initiated. The extent of completion of the demonstration will depend heavily on the pace of the implementation process. Since this is the first time this technology will have been sited at the pilot plant scale, the implementation process time table contains significant potential variations and unknowns. Initial design work for next generation plant will be completed.

#### **Transition Plan:**

A memorandum of understanding (MOU) between DON and DOE for exchange of technical assistance in environmental problems has been prepared and is being expected to be signed prior to the initiation of work. Personnel at potential demonstration sites have been contacted and are interested in this technology. All are willing to serve as the site of a field test. The user and regulators will be invited to participate at all stages of SCWO pilot plant development to ensure that their concerns regarding safety, cost, compliance, reliability, and other issues are addressed.

Most of the components of a SCWO system are common items in the chemical process industry. The expertise of the chemical process industry, commercial developers of SCWO, and technical experts from industry, government, and academia will be used as required to produce the pilot plant.

#### **Funding: (\$K)**

	FY93	FY94
SERDP	900	2,500
DOE	1,600	2,500
Total	2,500	5,000

**Performers:**

Agency:	Performer:
Navy	Naval Civil Engineering Laboratory
DOE	Environmental Restoration and Waste Management

**Industry Involvement:** The expertise of the chemical process industry will be drawn upon for detailed design and construction of the SCWO pilot plant.

**Planned Cooperative Development Agreements:** Opportunities for Cooperative Research and Development Agreements will be pursued when such agreements support the overall goals of this project and do not restrict free and open development of SCWO technology. Specific cooperative development agreements with industry and universities are expected to be identified after initiation of this project.

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\* Note: The SERDP Scientific Advisory Board provided specific guidance to this project. Their position statement on this effort may be found in a separate section within this document; see "Table of Contents."

## SERDP Thrust Area: Compliance

### Title: Kinetic Mechanisms for Supercritical Water Oxidation

#### Problem Statement:

Supercritical, water oxidation is an emerging technology under development by numerous laboratories and industries for the treatment of hazardous aqueous wastes. The process is performed at temperatures and pressures above the critical point of water (typical process conditions: 500-600 °C and 240 bar), and is applicable to waste streams containing 0-20 percent organics in water. A wide variety of organics is efficiently destroyed (destruction and removal efficiencies better than 99.99%) in residence times of less than a minute.

Previous studies have shown that global mechanisms are of limited use in the formulation of a predictive model of SCWO rates. They appear to be constrained to simply describing experimental results in a compact form and do not extrapolate well to pressure, concentration, and temperature regimes that have not been directly measured. In industrial applications, this technology will be faced with handling feeds of widely varying concentration and equipment will be operated at varying temperatures. Operators wishing to achieve high waste destruction efficiencies will need to be able to anticipate final concentrations of chemically robust species such as methane and methanol. To obtain this predictive capability, reaction models will need to be based on elementary reaction steps.

At typical operating conditions, supercritical water is about a tenth the density of liquid water and exhibits physical characteristics of both liquids and gases. Most important is its behavior as a solvent. Many organic materials are miscible in all proportions, as are the combustion gases such as O<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub>. As a result, oxidation reactions proceed in a single phase without the delays associated with interphase transport. Operation at densities two orders of magnitude greater than atmospheric gaseous combustion provides high reaction rates at moderate temperatures. Yet density is low enough that mass diffusivity remains favorably high and viscosity low compared to liquids.

Most experimental studies to date have performed bench-scale measurements of overall destruction efficiencies for a variety of waste chemicals. An early patent for the process included data showing 99.99% destruction of many normal and halogenated hydrocarbons including tetrachloroethylene, DDT, and PCB. Since then, the number of organic and inorganic chemicals, as well as complex mixtures, treated by SCWO has grown considerably. Industrial sludges have been successfully treated by several researchers to yield reusable water, clean gases, and inorganic solids. Experiments performed at Sandia demonstrated effective destruction of the organic components of a simulated DOE mixed waste (radioactive plus organic waste). In the general class of studies outlined above, output streams were sampled, analyzed, and the results were compared with feed concentrations to calculate the percent of feed material destroyed. Data like this can be used to generate global kinetics mechanisms.

Although *in situ* measurements, particularly of unstable intermediate species, could provide valuable information for understanding SCWO kinetics, no such published data is available. Optical measurement techniques have been successfully demonstrated in supercritical water;

for example Raman spectroscopy has been used to measure chemical interactions, composition, and temperature in this environment. To date, however, no one has applied such techniques to measure the progress of reactions in supercritical water. Data obtained *in situ* eliminates uncertainties associated with sample and analyze techniques as well as offering the unique potential to measure unstable species.

### Project Description:

This project will establish experimental capabilities and make initial *in situ* measurements on fuel species and partial oxidation products in an optically accessible supercritical water oxidation (SCWO) reactor. The work proposed here continues this experimental approach, begins measurements on key oxidant species, and expands the variety of experimental methods, primarily optical in nature, that can be used to study reactions at these conditions. The second phase of the project will improve the existing detailed elementary reaction mechanism for the oxidation of methane and methanol. Raman and absorption spectroscopic techniques will be utilized to generate concentration vs. reaction time profiles for the oxidation of methane and methanol by oxygen and hydrogen peroxide. The thermal decomposition rate of hydrogen peroxide will be independently measured at typical oxidation reaction conditions. These experiments all focus on measuring the primary oxidation steps that involve the hydroxyl and HO<sub>2</sub> radical, generating data which will be used to evaluate and refine SCWO reaction kinetic schemes.

The proposed study of reaction kinetics in supercritical water undertakes *in situ* measurements of reactants, intermediates, and products in order to provide unambiguous experimental results for evaluating reaction kinetic mechanisms. Research in the combustion field has highlighted a wide variety of optical spectroscopic techniques that can be applied to reacting flows to identify and quantify molecular species present. This project will focus on using *in situ* optical techniques to measure the primary oxidation steps that involve the hydroxyl radical. The resulting data will be used to evaluate and refine SCWO reaction kinetic schemes.

This proposed project will investigate the currently uncertain chemical kinetics of supercritical water oxidation. Numerous experiments have demonstrated that SCWO efficiently converts many wastes to small, harmless molecules, but little data is available to elucidate the elementary kinetics of the process. Simplified reaction mechanisms have been proposed but they fail to satisfactorily predict the experimental data. We propose a program of experiments and modeling designed to improve our understanding of and ability to predict SCWO chemistry.

The experimental portion of the research entails determining the concentration of reactants, stable intermediates, radicals, and products associated with the oxidation of simple fuels in supercritical water. Concentration profiles of abundant species will be measured *in situ* in a supercritical flow reactor using spontaneous Raman spectroscopy. The measurement of trace species will require application of more sensitive optical methods that will be adapted and applied as a part of this project.

The modeling portion of the project will improve existing elementary reaction mechanisms by incorporating data measured in the experimental portion. Initial investigations of the

inadequacies of mechanisms previously proposed for supercritical environments will guide the design of experiments. Subsequently, the results of the experiments will be used to improve the predictive performance of the models and theoretical corrections to reaction kinetics for high-density effects will be applied.

Ten months after starting the initial funding of the project a picture of the concentration-time profiles will be generated for methane, carbon monoxide, carbon dioxide, and oxygen at one reaction temperature near 530 °C and at pressures of 240 bar, 300 bar, and 400 bar. These results will be obtained by monitoring individual species using spontaneous Raman spectroscopy in the flow reactor. Concurrently, a modeling team will be tailoring the detailed kinetics mechanism for application at SCW densities.

The effect of our experiment's threefold change in density on reaction kinetics will then be evaluated. A high-pressure, remote-actuated sample valve will be installed in the flow reactor during this segment of work. It will be used to collect samples for gas chromatographic or mass spectrometric analysis. The results from rapid sample-and-quench studies will be compared to the optically obtained data.

After the study of stable molecules at a single temperature is completed, the focus will shift to measuring  $\text{H}_2\text{O}_2$  and OH first in the cell reactor and then in the flow reactor. The study on stable reactants to higher pressure (up to 500 bar), and to 625°C will simultaneously be expanded. A sensitivity analysis of the kinetics mechanism will indicate which elementary reactions most affect the model's predictions. As experimentally measured profiles for different reactant concentrations and reactant conditions become available, the modeling team will be able to further refine the set of reactions that make up their kinetics mechanism.

#### **Expected Payoff:**

Supercritical water oxidation is a rapidly developing waste treatment technology that has potential application to a wide variety of military and industrial materials. Past experience from applied testing of industrial chemical waste has shown that complete oxidation of complex organic material is limited by the oxidation rates of small molecules such as methanol, methane, hydrogen, and ammonia. The ultimate effectiveness of this technology will rely on the production of a final effluent for disposal that is sufficiently clean to require no further treatment prior to disposal. As a result the success of this technology hinged on optimizing the oxidation of simple molecules, not complicated ones. Results from this study can be applied directly to optimizing overall engineering design parameters such as oxidant concentration, optimum temperature, and required residence times.

#### **Milestones:**

The following outline illustrates items to be accomplished in FY93:

1. Improve existing detailed reaction mechanism to incorporate high density parameters, building on and attempting to reproduce results on methane from FY 1993 experimental studies.
2. Extend pressure dependence measurements on methane oxidation.
3. Develop absorption techniques for detection of intermediates in cell reactor.

4. Measure hydrogen peroxide decomposition rates at supercritical temperature and pressure.
5. Install and operate remote sample valves and compare results to optical measurements.

**Transition Plan:**

Three groups that have made considerable progress in supercritical research, in both experimental and modeling areas, are Professor J. Tester's group at MIT, Professors M. Klein, T. Brill and associates at the University of Delaware, and Professor K. Johnston and associates at the University of Texas. Tester's work has emphasized reaction kinetics and modeling of simple systems and has met with success in modeling H<sub>2</sub> and CO oxidation. The Delaware group has focused on optical methods in supercritical water and published and first Raman spectra in this medium. Johnston's work has emphasized a molecular level approach to solvent effects in the supercritical fluids.

As experimental results are obtained, details of species concentrations will be compared with these existing models. The sensitivity of the concentration of individual species to activation energies and preexponential factors, and to reaction conditions will be determined and the kinetics model will be refined. Of special interest is the typically observed zeroth order dependence of reaction rate on oxygen concentration.

**Funding: (\$K)**

FY93  
490

**Performers:**

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## **SERDP Thrust Areas: Compliance**

**Title:** Advanced Testing of Emissions Produced During Open-Air Destruction of Energetic Materials

### **Problem Statement:**

The goal of this project is to characterize emissions produced by open-air detonation of energetic materials and to recommend means for improving the efficiency of this type of detonation. As deficiency increases, the quantity of undesirable emissions are expected to decline. Although the energetic materials in this program will consist primarily of propellant, explosive (including munitions), and pyrotechnic (PEP) materials, other items can be accommodated.

The substantial amounts of PEP materials accruing within the DoD have become an increasing burden on the military logistics system. Storage facilities are now saturated, huge amounts of these materials are scheduled for retrograding to CONUS from overseas locations, and environmental regulators are demanding item-specific data before allowing their destruction in a manner which releases combustion products into the atmosphere. These data are not available. Until new permits are granted, or existing permits extended, a dangerous situation will be aggravated.

This project, which proposes to develop the means for grouping PEP items in the demilitarization stockpile into emission families, is a new project.

### **Project Description:**

This project is intended to provide the means of characterizing emissions from all PEP items in the DoD demilitarization inventory, group these items into emission families to allow disposal efficiencies, and provide data acceptable to the U.S. Environmental Protection Agency and state regulators for permitting purposes. Chemical and smoke munitions are specifically excluded from his research effort.

The technical approach consists of identifying PEP items which should be characterized by emissions, developing the means to test these items, conduct tests, assaying samples collected during testing, relating the results to environmental standards, classifying PEP items by emission families, and developing an open-air destruction dispersion model with subsequent laboratory validation of the model.

This project directly supports the DoD objective of avoiding environmental injury during conduct of military-related operations. Results will identify which items in the demilitarization inventory may be subjected to open-air destruction without damage to the environment and which items require an alternate-technology disposal system. Dugway Proving Ground knows of no similar work which is on-going.

Technical investigators will begin a comprehensive review of PEP material contained in the DoD demilitarization inventory and identified in the Joint Ordnance Commanders Group Demilitarization/Disposal Handbook, Volume 1, Demilitarization/Disposal Inventory



(commonly referred to as the "Orange Book"). They will select items for testing which are likely to be good environmental candidates for open-air destruction, appear to have the potential of being grouped into emission families, and for which destruction will produce a high dividend.

The project officer will review the list of nominated munitions and determine what modifications must be made to existing testing facilities, instruments, and procedures. Factors to be considered include: type of explosive, amount of explosive, ancillary munition components, normal disposal techniques, anticipated emissions, and safety requirements. The supporting technical team will prepare a list of target analyses for each item. Appendix 9 compounds will be represented as appropriate, and other compounds of concern will be included if their generation appears likely.

Detailed procedures will be developed which specify means of preparing items for testing, detonating or burning the item, collecting samples of gases, and airborne particulates. Principal analytical methods will include real-time gas analyses using EPA-approved gas monitors, supercritical fluid chromatography/mass spectrometry, gas chromatography/mass spectrometry, inductively coupled plasma mass spectrometry, and pyrolysis. Emerging technologies such as atmospheric pressure ionization time-of-flight mass spectrometry will be used to augment the more traditional instruments.

Statistical analysis will normalize all test results and determine emission factors of each munition. Emission factors will be presented in a manner suitable for subsequent calculation of total emissions of specific compounds that will be produced during large-scale open-air destruction operations of each tested item. These emission factors will also be suitable for use in the open-air destruction downwind dispersion model.

The program manager will review conceptual designs of a ventilated underground chamber which will contain large explosions and permit sampling of emissions produced by large munitions undergoing open-air demolition. When the ventilation system is disengaged and munitions are covered with dirt, it will allow sampling of emission produced during underground (buried) detonations, a procedure used by many DoD disposal activities.

#### **Expected Payoff:**

Initial users are expected to be all elements of the DoD, including the reserve component, state national guards, and the EPA. As the EPA expands its requirement for emissions data, ammunition and propellant manufacturers will ask to be included in the testing program.

Open-air treatment of PEP materials is the fastest, least expensive, safest, and only on-line means of disposing of most unwanted items. Data produced as the result of this project should provide the means of obtaining environmental permits for open-air destruction of a large percentage (possibly 75 percent) of the demilitarization inventory.

Funds will not need to be allocated for developing special facilities or item-peculiar equipment for items identified as being suitable for open-air destruction. Conversely, funds can be efficiently directed to development of alternate destruction methods for items found not suitable of open-air destruction.

**Milestones:**

Projected accomplishment by 30 September 1993 are:

Instrumentation and data-acquisition system procurement (\$361,000)

Identification of Orange Book candidates for testing (\$27,000)

Testing 10 selected items (\$180,000)

Laboratory assay of samples (\$153,600)

Statistical analysis of laboratory data and report (\$80,000)

Determining feasibility of grouping items by emission (\$35,000)

Review of underground facility conceptual design (\$10,000)

Development and laboratory certification of open-air destruction dispersion model (\$100,000)

**Transition Plan:**

Testing activities conducted during FY93 will be more extensively pursued in FY94, assuming sufficient funding is received in a timely manner. The same personnel and facilities will characterize emissions from additional munitions with small explosive weights and small amounts of propellants. Concurrent with testing, final underground design selection will be made. Construction of the underground test chamber will be proximate to the DPG BangBox. No disruption of testing activities or project advancement will occur due to the stability of personnel. Continuing and complete coordination is being maintained between DPG and the US Army Environmental Center, Compliance Division, Aberdeen Proving Ground, Maryland.

**Funding: (\$K)**

FY93	FY94
568	278

**Performers:**

The DPB will direct and manage this project. The BangBox test facility, located on DPG, will be used to conduct all testing. DPG personnel will prepare items for testing, operate real-time instruments and data-acquisition systems, and prepare reports. Laboratories conducting sampling and assay include alpine West Laboratories (Provo, Utah), Oregon Graduate Institute (Beaverton, Oregon), and Radian Corporation (Research Triangle Park, North Carolina). Andrulis Research Corporation (Salt Lake City) will assist in planning, data analysis, and reporting.

**Technical Point of Contact:**

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## **SERDP Thrust Area: Compliance**

### **Title: Solar Detoxification of Explosives in Water**

#### **Problem Statement:**

The goal of this proposal is to develop a cost effective solar photochemical process that can reduce the level of contaminants in pink water to meet environmental regulations.

Targeted organizations are military facilities having water contaminated with explosives and military facilities which operate processes that produce pink water or red water

There is a great need within DOE and DoD for new technologies that treat aqueous munitions waste. Production lines used to fill ordnance with explosives or to decommission devices containing explosives generate large volumes of waste water. This is termed pink water - water which is typically contaminated with dilute concentrations of TNT, RDX, and HMX. In addition to these process-generated waste water streams, at some sites the contamination has found its way into the groundwater.

In the past, the method of cleaning contaminated waste streams and groundwater was to contact it with carbon, which adsorbed the explosive. When the carbon was saturated with explosive, it was taken to a controlled area and burned. It does not appear that adsorption will be able to reduce TNT to the levels required by new standards for discharge of water. In addition the spent carbon can no longer be burned in open pits. Now the carbon must either be regenerated or sent to an incinerator and destroyed per EPA regulations, resulting in a significant increase in cost. Thus, cost effective methods must be found for treating explosives-contaminated process streams as well as explosives-contaminated groundwater. While the contaminated groundwater must be dealt with on a site-by-site basis, eliminating explosives-contaminated water effluent from the various munitions processes will deal with the problem at its source and is the long-term solution to the problem. The Army is looking for a new technology that can provide this solution.

Alternative Technologies: Treatment of pinkwater streams at load and pack (LAP) facilities and contaminated groundwater having similar compositions is required at a number of sites across the country. These have been documented in a recent report. A wide range of possible treatment processes has been investigated over the last two decades. Examples include super critical water oxidation, improved adsorption processes, ultraviolet (UV)/hydrogen peroxide, UV/ozone, and biological methods. However, these processes are more expensive than carbon adsorption and there are various performance limitations. The challenge, therefore, is to develop a cost-effective process that reduces the concentration of nitroorganic compounds to acceptable levels and does not leave by-products in the water that are themselves unacceptable. This may ultimately dictate a process that is comprised of more than one unit operation.

Experimental work conducted by the DOE and elsewhere has shown that photocatalytic oxidation can be used to successfully destroy a wide range of organic compounds in water. The process does not require the addition of other reagents such as ozone or hydrogen peroxide and can operate under sunlight or lamps so it has the potential to be of lower cost

than others that have been studied. The relative costs of photons from lamps and sunlight have been compared and the solar option is competitive at sites throughout the U.S.

The photocatalytic process uses a semiconductor catalyst such as titanium dioxide ( $\text{TiO}_2$ ) in conjunction with near UV light to generate strongly oxidizing and reducing species. Use of the process to destroy TNT in water has been shown with mixed results. While some research has produced evidence for effective removal of TNT, others have found only partial success. The difference may lie in the susceptibility of TNT and related compounds to both oxidation and reduction. Preliminary experimental results support this idea. Reductive chemical processes have received very little attention so this opens a new pathway for solving the pink water problem.

This would be a new program, but would leverage a similar program being sponsored by the DOE which is developing solar photochemical technology to destroy other hazardous chemicals in water

### **Project Description:**

The proposed project is an applied research and development effort to determine the potential for using a photocatalytic process to destroy explosives in pink water and evaluate the use of solar energy as the photon source.

Laboratory research will provide data needed to establish the feasibility of using a photocatalytic process to destroy the hazardous compounds in pink water. The following approach will establish the processing conditions which lead to destruction of the compounds in pink water and provide the basis for assessing the costs of using solar energy as the light source for the process. The technical approach will consist of:

performing laboratory feasibility and optimization experiments,  
performing outdoor experiments to verify the indoor results and,  
developing a systems model based on performance data generated from indoor and outdoor experiments.

Data from this work will provide the basis for cost estimates and the design of a pilot plant if the decision is made to go to the next stage of development. This information will allow the Army to decide on the merits of using a solar photocatalytic process to address its problem of explosives-contaminated water. To collect this data, the National Renewable Energy Laboratory (NREL) and Sandia National Laboratories propose the following tasks:

#### **Task 1. Laboratory Research**

**1.1 Oxidative Chemistry:** Experiments will be carried out to establish the conditions which maximize the destruction of the nitro-compounds found in pink water. These experiments will be conducted using near UV photons generated from electric lamps.  $\text{TiO}_2$  will be used as the photocatalyst with air, pure oxygen, and hydrogen peroxide as the oxidizing agents to be tested.

**1.2 Reductive Chemistry:** Limited experiments performed at Sandia has demonstrated that

reductive chemistry may play an important role in destroying nitro-compounds in pink water. Further experiments will be carried out to establish the extent to which reduction of the nitro-compounds in pink water may play a role in the photocatalytic process.

1.3 Process Optimization: After performing initial feasibility experiments in Tasks 1.1 and 1.2, researchers will determine the conditions which are most effective for the removal of the hazardous components of pink water. These optimization experiments will be performed using both spiked deionized water and actual pink water.

1.4 System Integration: System integration is often overlooked when developing new waste treatment technologies. However, if given due consideration prior to and during the research and development phases, then the likelihood for success of the new technology can be greatly enhanced. Pretreatment may be necessary if the pinkwater exhibits high turbidity or opacity in the near ultraviolet.

## Task 2. Conceptual Design and Systems & Economic Analyses

The objective of Task 2 is to determine if photocatalytic oxidation and/or reduction is in general a cost-effective method of removing the toxic compounds contained in pink water and, specifically, to determine if sunlight is a cost-effective source for the necessary UV photons. In this task, researchers will develop a (1) kinetic model based on laboratory results, (2) a conceptual design(s) for a continuously operating solar system, and (3) a systems model based on the design to perform cost estimates.

2.1 Development of a kinetic model will run concurrently with Task 1. The model will account for important process parameters such as concentration of reactant, UV intensity, Ph, etc. Various models will be tested during the accumulation of data generated from the laboratory feasibility and optimization experiments.

2.2 Conceptual Design(s): After validating the kinetic model, researchers will formulate conceptual design(s) for the system based on the process kinetics, expected flowrates, and operating constraints. Questions regarding process control, continuous operation, solar/UV lamp hybrid configurations, etc. will be addressed.

2.3 System Model and Cost Estimates: Once the conceptual design has been completed, major system components can be identified and costs estimated. A system model will be developed based on the kinetic model and conceptual design to produce annualized cost data, including capital and operating expenses, for the treatment system.

## Task 3. Outdoor Testing

The objective of task 3 is to verify that laboratory-scale experiments provide a reasonable method for predicting outdoor performance and to test samples of pink water from a plant selected in consultation with the Army. The laboratory experiments conducted under Task 1 will provide much of the necessary information needed to estimate the cost of large-scale systems as defined in Task 2. However, this cost estimate will rely on extrapolating the laboratory data to account for differences in reactor configuration, spectral distribution, illumination intensity, simulated v. real pink water, and other parameters characteristic of

large-scale systems.

**3.1 Modify Test Equipment:** All of the experiments performed in Task 3 will take place at NREL's Solar Industrial Mesa Test Area (SIMTA). Researchers will take advantage of equipment already installed at the site for investigating the solar photocatalytic detoxification of hazardous wastes in water, however, some modifications may be necessary to address materials compatibility or safety issues. The test area is equipped with concentrating and nonconcentrating photoreactors and ancillary equipment such as pumps, tanks, and instrumentation necessary to fully support outdoor treatability experiments.

**3.2 Validation Experiments with Simulated Pink Water:** After modifying the test equipment, researchers will conduct a small number of experiments outdoors on simulated pink water. These experiments will consist of treating 5 to 30 gallon batches of water over a period of approximately one hour. The experiments will be performed at the conditions identified in the laboratory which result in optimum performance of the process. Results from these experiments will be compared to the results predicted by extrapolating the laboratory data to the larger scale system.

**3.3 Outdoor Treatability of Army Water:** Outdoor treatability experiments on actual pink water will provide information which is essential to completing a final cost estimate for the solar photocatalytic process. Again, these experiments will be performed at the optimum conditions established in the laboratory and earlier outdoor experiments. In addition, any pretreatment and posttreatment requirements identified in Task 2 will be used to ensure that the data collected will fully represent the end result of an integrated system.

#### Task 4 Reporting

Quarterly reports will be sent to the SERDP Program Office and the appropriate Army R&D group (AEC, WES, or CERL). Results of the experimental work, the demonstration system, and the economic analysis will be given in a final report. Results will be presented to the Environmental Center and the SERDP Office. Quarterly meetings will be held.

**Relationship to DoD/DOE Environmental Objectives -** Explosives contaminating water at military facilities is one of the Department of Defense's (DoD) most serious environmental problems. There are numerous Army munitions facilities in the United States that have water contaminated with explosives and propellants. The DoD's goal is to find a less costly alternative method of cleaning the water to that of carbon adsorption and incineration. Existing incineration technology requires high temperatures to destroy the gases desorbed from the carbon. This requires a great deal of energy and may result in hazardous byproducts. By using the photocatalytic process, solar energy may be able to safely and completely destroy the contaminants at ambient temperatures. This may lead to an inexpensive method of destroying the explosives. The use of solar energy also provides a clean energy source that does not cause unwanted air emissions, acid rain, or contribute to global warming.

**Relationship to other similar ongoing work -** DoD, EPA, and DOE have formed a cooperative Tri-Agency Project to demonstrate the use of solar energy to remediate contaminated soil. In particular, it is aimed at the destruction of volatile and semi-volatile organic compounds

contaminating soils at Army facilities. A system demonstrating the solar concept is planned to be operating at the Sierra Army Depot in California by FY94/FY95. In the Tri-Agency Project, explosives have been explicitly removed from consideration. The Tri-Agency project treats contaminants in the gaseous medium. Therefore there is no overlap between the Tri-Agency Project and the work proposed herein.

The Department of Energy has a program that is supporting the development of solar technology to detoxify hazardous organic wastes in water. Laboratory results show that solar energy effectively destroys a number of solvents, pesticides, and dyes. These data have been confirmed in a field experiment at a Superfund site in Livermore, California during 1991. The experiment showed that a solar process could destroy, to EPA standards, trichloroethylene that had contaminated groundwater. A second field experiment was recently completed at the Tyndall Air Force Base in Florida in which the solar photocatalytic process was used to destroy jet fuel in contaminated groundwater. These results have resulted in substantial industrial interest, and several small companies are currently developing the first commercial systems.

Technical risks - the process of solar detoxification of water is based on a body of work in semiconductor photoelectrochemistry that has been developed over the last two decades. It is well established that a wide variety of organic compounds can be completely mineralized (broken into carbon dioxide, water, and mineral acid) in water over polycrystalline semiconductors when they are irradiated with light exceeding the band gap of the semiconductor energy. These uncertainties will be addressed by the proposed work.

#### **Expected Payoff:**

Benefits - this may result in a technology that the DoD and DOE could use to solve some of its most serious environmental problems. Solar technology could help clean groundwater contaminated with explosives (pink water).

As side benefits, the solar detoxification process will destroy a wide variety of hazardous organic chemicals (solvents, pesticides, and dyes) that may be included in the groundwater or process wastewater. The process may also remove some heavy metals from water. This may result in significant long-term savings to the DoD.

#### **Milestones:**

(Months from start of project)

Six-month Progress Report	6 months
Oxidative and reductive chemistry tests complete	12 months
Process optimization tests complete	15 months
Process integration study complete	15 months
Kinetic model complete	15 months
Outdoor validation and real water tests complete	16 months
Develop conceptual design of detox system	17 months
Complete system model cost estimate of detox process	19 months
Submit final report	20 months

**Transition Plan:**

Next step - This project will provide the basis for a new process to treat pink water. The data could be used to design a pilot plant that could be built and operated at a DoD site. It will be supported with laboratory data establishing the destruction rate of the explosives and a cost estimate of the process. The information from a pilot plant, if successful, could be used to complete a design for a full scale system and a cost estimate of that system. This would enable the Army to determine if it wants to build a full scale plant at an Army facility.

Coordination - The DOE will be responsible for coordinating the project management with the SERDP program and the Army (THAMA, CERL, and/or WES). The National Renewable Energy Laboratory (NREL) would be the technical coordinators of the project; acting as liaison between laboratory engineers, the industry sub-contractor, and the DOE/Army management team. The goal of the DOE in this project is to use solar technology to solve a problem of interest to the DoD. Achieving this goal requires close cooperation between all of the above mentioned organizations. The task descriptions were developed with this philosophy.

**Funding: (\$K)**

FY93  
890

Funds other than those allotted for subcontracts will be used at NREL or Sandia National Laboratories.

**Performers:**

DOE: NREL, Sandia  
SERDP: THAMA, CERL, WES

**Technical Point of Contact:**

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## **SERDP Thrust Area: Compliance**

**Title:** Hydrothermal Reduction of Eroded and Intact Energetic Wastes

### **Problem Statement:**

The goal of this project is to develop hydrothermal reduction as a safe, nonpolluting method for disposal of waste solid rocket propellant from manufacture, refurbishment, and demilitarization of large rockets and for disposal of selected Army, Navy and Air Force conventional munitions including those containing explosive D. Hydrothermal reduction could serve as the primary treatment step in the disposal of solid rocket propellant and other energetics or as a pretreatment for supercritical water oxidation. If employed as the primary treatment method, effluent from the hydrothermal reduction step would be treated by biological treatment or an advance oxidation process. Hydrothermal reduction also has potential for in situ (in the casing) decomposition of propellant and other energetic materials.

Activities having responsibility for disposal of waste propellant from rocket motors and energetic waste from demilitarization of conventional weapons. This would include all Tri-Service activities, USADACS, AMCCOM, USN/SSP and the Air Force Material Command, Ballistic Systems Division (BSD) as well as Ogden Air Logistics Center responsible for Air Force large rocket motors. This technology could apply to projects under investigation by the DOE, such as the Waste Component Recycle, Treatment and Disposal Integrated Demonstration and DOE/USAF Pollution Prevention and Waste Minimization Memorandum of Understanding.

Current incineration and open burning/open detonation methods generate air and solid pollution, require permits and site remediation, and are at risk for increased regulation and possible shutdown. The wet air oxidation and supercritical water oxidation operating regions have been explored in other efforts. However, destruction of energetic materials, which are characteristically oxidant rich, in near critical water under reducing conditions (hydrothermal reduction) has received little attention. In a previous 6.2 effort, decomposition of individual energetic materials into smaller, nonenergetic molecules under conditions of hydrothermal reduction was verified in bench scale experiments, and the catalytic effects of certain salts was discovered. The method, hydrothermal reduction, decomposes energetic wastes in subcritical water at temperatures ranging from 250°C to 373°C (the critical temperature). Corresponding pressures required to maintain the liquid phase range from 580 psi at 250°C to 2400 psi at 350°C with a maximum of 320 psi as temperatures approach 373°C. The chemistry appears to change from hydrolysis to reduction at higher temperatures. Reducing agents, but not oxidants, are added depending on the material to be treated.

This project is a new start in 1993.

### **Project Description:**

The technical objective of this program is to develop and demonstrate hydrothermal reduction for destruction of propellant and other energetic wastes, first at bench scale and then at the prototype scale. Hydrothermal reduction will be applied to both continuous processing of propellant wastes and to destruction of propellant in the rocket motor casing.

Treatment methods for hydrothermal reduction effluent, whether from continuous processing or from in-situ propellant decomposition, will be integrated with the technology. Methods to be investigated for integration with hydrothermal reduction are advanced oxidation (ozone/hydrogen peroxide/UV), biological treatment and supercritical water oxidation.

The technical approach can be classified into four areas: bench-scale tests, demonstration of continuous processing, in situ destruction of propellant and effluent treatment technologies. Bench-scale tests will be run to expand the experimental database. Tests on pure materials will expand the database to higher temperatures, increased concentrations and additional energetic materials including ammonium picrate and to provide a better understanding of catalytic effects. A second set of experiments will test decomposition of composite propellants and energetic mixtures. Continuous processing will be demonstrated in a bench-scale reactor, which will be constructed and operated as part of this project. Preliminary batch scale experiments will determine whether hydrothermal reduction has potential for application to smoke and dyes. Based on the bench-scale results, a continuous prototype reactor can be constructed and tested.

In situ (in the casing) decomposition will be evaluated by performing bench scale experiments on solid blocks of propellants and composites. If the course and rate of in situ propellant decomposition and removal of reaction byproducts are promising, in situ decomposition will be demonstrated on a subscale motor.

A literature search will be conducted to locate information and commercially available equipment applicable to conventional aerobic biological treatment and advanced oxidation processes. Tests will initially be performed on a solutions mixed in the lab and later on actual effluent from the bench scale reactor. Lab tests will be conducted on promising advanced oxidation processes/systems to identify and overcome any barriers to operation at high temperatures. Treatment processes will then be tested in a continuous bench-scale system. For biological treatment, organisms from sewage treatment sludge will be tested for degradation rates and the most promising cultures will be enriched. Continuous operation will then be demonstrated in a bench scale system. Depending on the results of the lab experiments, advanced oxidation may be integrated into the prototype hydrothermal reduction system design. Biological treatment would use conventional technology and therefore would not necessarily be demonstrated in a prototype unit. Hydrothermal reduction will be evaluated as a pretreatment for supercritical water oxidation by performing sequential tests under conditions of hydrothermal reduction and then supercritical water oxidation.

Hydrothermal reduction promises a safe, economical nonpolluting method for disposal of solid rocket propellants and energetic material from conventional munitions. Development of alternatives to open burning/open detonation are critical if DoD is to fulfill propellant disposal requirements in an environmentally acceptable manner.

This effort will exploit other activities focused on the destruction of energetic materials. Removal of Class 1.1 propellant by cryogenic washout and disposal by supercritical water (SCWO) are being demonstrated at prototype scale under contract with General Atomics. Small scale destruction of waste laboratory energetic materials by hydrothermal reduction will be tested in a separate 6.2 effort. Hydrothermal reduction can serve as a method to

expedite these processes or may prove to be a more economical method of SCWO pretreatment. SCWO is also being tested by ARPA for disposal of hazardous wastes and by DOE for mixed wastes. Research on the disposal of energetic materials ongoing at Los Alamos and Sandia National Laboratories on SCWO high temperature corrosion and solids formation will contribute to the research surrounding hydrothermal reduction.

Although accompanied by technical risks commensurate with any R&D project at a similar stage of development and similar complexity, development of hydrothermal reduction reduces the overall risk in the search for alternatives to open burning/open detonation. Reaction paths and the basis for catalytic effects are not well understood at this time. Further testing at higher temperatures, in the presence of catalysts and on energetic mixtures may not be as predicted. In situ destruction of propellants might prove impractical due to mechanical complexity, slower than expected reaction rates, solids sloughing and plugging, etc. Technical risk in treatment of hydrothermal reduction effluent is mitigated by pursuing three possible technologies; advanced oxidation, biological treatment and supercritical water oxidation. All three are technically achievable, but could prove impractical or uneconomical.

#### **Expected Payoff:**

Development of hydrothermal reduction promises a safe, economical and environmentally acceptable method for disposal of solid rocket propellant and energetic material from conventional munitions, smokes and dyes. Biological treatment or advanced oxidation processes will serve as the final treatment prior to discharge. Hydrothermal reduction can be used as a pretreatment step for supercritical water oxidation, which is at the prototype test stage, replacing other pretreatment options such as acid or base hydrolysis. In situ decomposition of propellant could eliminate the need for a washout step and thus provide for more economical removal of propellant from the casings.

#### **Milestones:**

Based on laps time following receipt of funds (ROF).

Task I.	Bench Scale Testing	
	Contract for Bench Scale Tests	30 days
	Build Continuous Bench Scale Reactor	150 days
	Complete Tests on Individual Energetics	16 months
	Complete Tests on Blocks of Composites	28 months
	Complete Continuous Tests on Composites	31 months
	Technical Report	32 months
Task II.	Demonstrate In Situ Decomposition	
	Contract Award	30 months
	Engineering Design	34 months
	Assemble/Test Equipment	39 months
	Testing and Demonstration	46 months
	Technical Report	48 months

Task III.	Demonstrate Continuous Processing	
	Contract Award	35 months
	Engineering Design	42 months
	Prototype Construction	46 months
	Shakedown and Operational Tests	50 months
	Prototype Test and Demonstration	58 months
	Final Report	60 months
Task IV.	Biological Effluent Treatment	
	Start Work	12 months
	Batch Tests/Select Organism	21 months
	Continuous Bioreactor Operation	29 months
	Engineering Evaluation	33 months
	Technical Report	35 months
Task V.	SCWO Tests	
	Contract Award	18 months
	Test Representative Hydrothermal Effluent	23 months
	Test Actual Hydrothermal Effluent	34 months
	Technical Report	35 months
Task VI.	Advanced Oxidation	
	Literature and Process Survey	15 months
	Initial Process Selection	17 months
	Bench Scale Tests	27 months
	Oxidation Process Down Selection	28 months
	Bench Scale Testing	37 months
	Technical Report	39 months

#### **Transition Plan:**

The technology will be transitioned to OO-ALC for implementation in propellant disposal. For application to conventional munitions, the technology will be transitioned to the responsible Army, Navy or Air Force organization for implementation.

#### **Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
390	1250

#### **Performers:**

SRI International (Menlo Park, CA) will perform work on hydrothermal reduction. The work will be performed under an option being included in a project addressing laboratory energetic wastes. Work on biological treatment will be performed inhouse by ASI under the SETA contract. Advance oxidation treatment will be performed under a Task Order Contract or other appropriate mechanism. One of the organizations performing SCWO research (ARPA, General Atomics, etc.) will perform the SCWO treatment under an appropriate

contracting mechanism.

Planned cooperative/coordinating agencies: USADACS, USN/SSP, AFMC, OO-ALC, AMCCOM, DOE/OAK RIDGE, DOE/LOS ALAMOS NL, DOE/SANDIA NL, ARPA.

**Technical Points of Contact:**

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## **SERDP Thrust Area: Compliance**

### **Title: Catalytic Extraction Processing of Energetic Wastes and Munitions**

#### **Problem Statement:**

This project will develop Catalytic Extraction Processing (CEP) as a safe, economical, and environmentally acceptable method for the destruction of propellants, explosives, and pyrotechnic (PEP) wastes and selected munitions/components that cannot be recycled/reused for military or commercial purposes. The application of CEP to energetic wastes, munitions and metal components (fuzes, boosters, primers, etc.) containing energetic materials will destroy the hazardous organic constituent of the waste while generating useful metals that can be recycled/reused or sold for market value. Application of CEP would serve to replace current practices of Open Burning/Open Detonation (OB/OD) which is currently the primary treatment technology being utilized at ammunition production plants, load, assemble and pack (LAP) facilities, and installations with a designated demilitarization mission.

Targeted departments or organizations would be the DoD and DOE facilities with mission responsibilities for the disposal of energetic materials from conventional and non-conventional (e.g., rocket motors, warheads, etc.) munitions.

Existing technologies being utilized for the destruction of hazardous energetic wastes, assembled conventional munitions and munitions components are primarily limited to OB/OD and incineration. These practices are under considerable scrutiny as being environmentally unfriendly by the public and the Environmental Protection Agency. There is a technological need for alternatives to these current practices that are known to contaminate human health and the environment. Recycle/reuse of a majority of the compositions that are currently OB/OD or incinerated are desirable. However, in many instances throughout the life-cycle from initial production through demilitarization, recycle/reuse of the energetic will not be possible. CEP, developed by Molten Metal Technology, Inc, dissociates hazardous wastes into their elemental constituents by injecting them into a bath of molten metal at temperatures as high as 3500 degrees Fahrenheit. The bath composition is dependent on the waste material that is being destroyed but is usually iron, nickel or copper. The process does not produce products of incomplete combustion that can form oxides of sulfur or nitrogen because of the reducing atmosphere inside the molten metal bath. Organic wastes containing inorganics and heavy metals are broken down into their respective elemental constituents of carbon and hydrogen, the metal is collected in the bath, while the inorganic forms a slag in the center of the bath. Gases generated from the bath contain carbon monoxide and hydrogen which can be recovered for industrial use or burned onsite for their BTU value. The inorganic slag can also be removed and sold for its commercial value.

This project is a new start in 1994.

#### **Project Description:**

Execution of this program will develop CEP technology as an environmentally acceptable treatment method for the destruction of energetic materials, munitions and weapons

components. OB/OD will be minimized and potentially eliminated through successful development of this program.

Phase I of this technology development program will demonstrate the technical feasibility of utilizing the CEP for the destruction of various types of propellant, explosive and pyrotechnic formulations. Bench scale experimentation and testing will be performed utilizing a 100 pound bath of molten metal on small quantities of energetic simulants. A preliminary hazard assessment will be conducted prior to testing with various types of energetic formulations. Various methods (from solvent injection to bulk materials feeding) will be analyzed for feeding energetics into the molten metal bath. The optimum method will be identified and developed. Full scale characterization of all process effluents generated from the molten metal bath will be conducted in accordance with standard EPA tests. Concurrent with the bench scale feasibility studies, inert testing using uploaded munition items will be performed on an existing 2000 lb CEP unit. Preliminary design data will be generated from the inert testing for the full scale design of a prototype demonstration treatment unit processing 100 lbs per hour of waste materials. A preliminary economic assessment will be conducted to identify the projected treatment and technology development costs for pilot scale development.

Phase II of this program will initiate the development of the technical equipment design package for the 100 lb per hour demonstration treatment unit. An existing off the shelf computer process control software package will be modified and integrated into the design of the treatment unit. Experimentation will be conducted to optimize energetic feeding parameters and identify the optimum materials of construction for the demonstration unit. Standard off gas treatment equipment will be identified and incorporated into the design package. This equipment will be utilized to purify the high energy producer gas.

Phase III will finalize the characterization studies required in support of the design effort. The process equipment design package for the demonstration treatment unit will be completed. A test plan will be formulated for operational verification of the system. The plan will be implemented after fabrication of the equipment during operational testing and proveout. A site survey will be conducted to determine the optimum location for the unit. The final model systems hazard analysis will be performed. The required environmental permitting documentation will be prepared and submitted for approval.

The equipment fabrication and proveout efforts will be executed in accordance with the transition plan.

CEP processing of energetic wastes is an environmentally attractive alternative treatment method to OB/OD. Development of alternative treatment technologies are critical to the DoD and DOE mission.

Molten Metal Technology has recently been funded by the Department of Energy, Sandia National Laboratory (Albuquerque, NM) to evaluate CEP technology for recovering precious metals (e.g., gold, platinum, etc.) from circuit boards generated from nuclear weapons dismantlement. Efforts will be leveraged with the execution of this program to ensure efforts are not duplicated.

Results of the phase I feasibility studies and technology development costs will dictate whether or not this program will proceed to phase II design. This technology is a viable alternative to OB/OD and has been demonstrated for a variety of hazardous and toxic wastes (included are halogenated organic solvents, PCB's, cyanides, and complex substances containing heavy metals, etc.). A commercial size treatment unit consisting of 2000 lb molten metal bath has been constructed and is currently being tested for a wide variety of wastes.

#### **Expected Payoff:**

A safe, economical, and environmentally attractive treatment method for the destruction of energetic wastes, munitions and munition components.

#### **Milestones:**

Phase I	Contract Award	1 month
	Bench Scale Tests on Simulant	3 months
	Hazards Assessment	4 months
	Bench Scale Tests on Energetic Formulations	7 months
	Inert Munitions Testing on Industrial Unit	12 months
	Technical Report	13 months
Phase II	Contract Award	13 months
	Initiate Engineering Equipment Design	13 months
	Bench Scale Tests to Support Design	25 months
	Integrate Process Control into Design	28 months
Phase III	Complete Characterization Studies	28 months
	Final Equipment Design Package	36 months
	Final Systems Hazard Analysis	36 months
	Environmental Permitting Documentation	48 months
	Technical Report	36 months

#### **Transition Plan:**

The technology will be transitioned upon completion of the design package to the Ammunition Peculiar Equipment Section at HQ, AMCCOM for implementation demilitarization mission. This procedure is analogous to the transition plan currently being executed for the Supercritical Water Oxidation Technology Development Program. the technology will be transferred to manufacturing and LAP facilities with the DoD and DOE.

#### **Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
600	750



**Performers:**

Molten Metal Technologies, Inc., Waltham, MA  
(Have proprietary rights to the CEP technology)

Planned cooperative/coordinating agencies: DOE, Sandia National Laboratory, Albuquerque, NM, Mr. Ted Wheelis

**Technical Points of Contact:**

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## **SERDP Thrust Area: Compliance**

### **Title: ADVACATE Boiler Emission Control System**

#### **Problem Statement:**

The goal of this project is to augment with FY93 funds a demonstration of ADVACATE SO<sub>2</sub> control technology previously funded in Phase I by:

- o adding features for NO<sub>x</sub> control
- o adding air toxics control
- o extending testing and analyses to demonstrate NO<sub>x</sub> and air toxics reduction
- o preparing an engineering evaluation in final report that evaluates applicability and projected pollutant reductions at DoD facilities.

The ADVACATE process was developed by the University of Texas, Air and Energy Engineering Research Laboratory/EPA, and Acurex Environmental, Inc. as a low-cost SO<sub>2</sub> control process using a unique dry sorbent prepared from boiler fly ash and lime. The Tennessee Valley Authority has recently completed a 10 MW<sub>e</sub> field evaluation of ADVACATE and ABB-Flakt has been granted a license for ADVACATE application on utility boilers. In FY92, an ADVACATE SO<sub>2</sub> control system was selected for SERDP funding at a DoD boiler site. Recent ADVACATE research indicates potential for significant NO<sub>x</sub> and air toxics control by modifying ADVACATE chemistry and the process steps.

Development of the process to date has been directed toward pulverized coal boilers, although a few minor process modifications should make ADVACATE compatible with stoker firing.

The proposed program is an enhancement to a Phase I SERDP project and current EPA research on ADVACATE emission control technology.

#### **Project Description:**

The original technical objective of this project was to apply ADVACATE to a DoD stoker boiler to demonstrate effectiveness for the large industrial stoker boiler population which has been ignored by Clean Coal Technology programs. [The high carbon stoker fly ash requires different sorbent processing than utility boiler ash for effective SO<sub>2</sub> control.] FY92 funding was only one-half (\$1.345 million) that required to retrofit a 10-12 MW<sub>e</sub> equivalent boiler for 90% SO<sub>2</sub> control.

The current technical approach is to collect ash from candidate DoD boilers in early 1993, perform bench and small-pilot evaluations, and make a preliminary estimate of ADVACATE retrofit costs. Simultaneously, a pilot program at Southern Research Institute will evaluate NO<sub>x</sub> and air toxics control capabilities of ADVACATE which can be applied at the DoD site. If additional funding is available in 1993, site selection and detailed design may commence prior to construction in 1994.

Title XIII of the Energy Policy Act of 1992 requires DOE to demonstrate coal-based technologies which are more cost-effective than existing technology. Based upon the most recent Electric Power Research Institute (EPRI) study, ADVACATE is the lowest-cost SO<sub>2</sub> control technology capable of 90% SO<sub>2</sub> reduction.

In addition, the proposed program would allow compliance with any local or state SO<sub>2</sub> regulation over a wide range of coal sulfur content, or alternatively allow a flexible SO<sub>2</sub> "bubble" for a group of DoD boilers. The anticipated NO<sub>x</sub> reductions of 20-40% are not significant since few stoker boilers are subject to NO<sub>x</sub> regulations, but air toxics reductions could be very significant. We know of no similar work for the stoker boiler sector which is in dire need of low-cost emission control technology.

Proposed tasks/activities are discussed under Milestones, below. Technical issues include:

- Use of stoker bottom ash vs. fly ash for sorbent
- Location of injection point for NO<sub>x</sub> control
- Effectiveness of carbon in ash for mercury emission control

These will be addressed in FY93 pilot evaluations at AEERL, Research Triangle Park and Southern Research Institute, Birmingham, AL.

#### **Expected Payoff:**

This project will demonstrate a low-cost multipollutant control system for smaller coal-fired boilers which will be available via Government license to all DoD facilities and will be available to the private sector through the licensee, ABB-Flakt. Since this will be the only stoker facility with ADVACATE, the possibility exists for a DoD Cooperative Research and Development Agreement (CRDA) with ABB-Flakt to provide future data for process optimization and development support for sales to the private sector.

The impact of the proposed project will be space consumed for lime and sorbent storage, and additional solid waste generated. Time required for installation depends on the extent of dust collector modifications to handle and recycle increased solids loadings and would pose no problem if a seasonal boiler is selected for retrofit. The efficiency of steam generation should be relatively unaffected by the installation and operation of the ADVACATE system. Although no cost studies have been performed for stoker application, ADVACATE was the most cost-effective SO<sub>2</sub> control technology identified in the 1991 Electric Power Research Institute study for utility boiler applications.

#### **Milestones:**

The following milestones reflect completion dates for the activities described in the Project Description.

Site visits, ash samples	04/93
Bench/pilot simulations	07/93
NO <sub>x</sub> /air toxics results	09/93
Cost estimates/site selection	10/93

Detailed design	12/93
Commence construction	04/94
Complete construction	10/94
Baseline tests	12/94
Shakedown/Startup	03/95
Testing/monitoring complete	12/95
Final report	03/96

#### **Transition Plan:**

U.S. EPA/AEERL is currently coordinating this project with the Corps of Engineers' Construction Engineering Research Laboratory, which is assisting in site selection for the Phase I ADVACATE system.

At the completion of the SERDP program, a final report will be issued (3/96) which projects the performance and costs of ADVACATE for stoker-fired boilers. The licensee(s) will be expected to arrange with the DoD facility a Cooperative Agreement wherein the facility will be available for potential clients and possible testing on other coals as fuels for broader applications of the ADVACATE technology.

Since the ADVACATE technology uses a modest amount of commercially available components, industry production is not a concern.

#### **Funding: (\$K)**

FY93  
1,250

This project will be substantially leveraged by funding from EPA/AEERL, TVA, and ABB-Flakt, whose combined funds will contribute \$785K toward the Phase I and II programs. In FY93 SERDP funding of an additional \$1.25 million will allow adaptation of the proposed enhancements. The following is a funding breakdown of tasks for both Phase I and II programs:

<u>Activity</u>	<u>Funding Level</u>	<u>Source of Funds</u>
Site visits/sampling	15	EPA
Bench/pilot simulations	75	EPA
NO <sub>x</sub> /air toxics tests	125	EPA
Cost estimates	20	EPA/ABB-Flakt
Design	150	TVA/ABB-Flakt
Construction	1500	SERDP
Sorbent (lime)	100	SERDP
Pilot support	400	EPA/ABB-Flakt
Operation	350	SERDP
Testing/monitoring	400	SERDP
Engineering study	100	SERDP
Final report	150	SERDP

**Performers:**

AEERL (pilot plant support)

TVA (field pilot support)

ABB-Flakt (design/engineering), existing CRDA with AEERL

DoD (host site/facility operation)

Southern Research Institute (NO<sub>x</sub>, air toxics enhancements)

Acurex Environmental (pilot plant/fundamental chemistry)

University of Texas (pilot plant/fundamental chemistry)

Test Contractor: To be determined

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## **SERDP Thrust Area: Compliance**

**Title:** eSCRUB - The application of DNA pulsed power to electron scrubbing of flue gas to remove unwanted by-products.

### **Problem Statement:**

Utilizing electron beam dry scrubbing (EBDS), the objectives of this program are to demonstrate a cost effective approach for removing  $\text{NO}_x$  and air toxins from DoD incinerators and  $\text{SO}_2$  and  $\text{NO}_2$  from coal fired boilers. This program will also provide technology transfer so that civilian utilities which use high sulfur content coal can continue to do so and still comply with the Clean Air Act Amendment (CAAA) of 1990. Thus, this program will avoid the devastating economic impact of the CAAA on producers of high sulfur content coal.

### **Project Description:**

The Defense Nuclear Agency has supported pulsed power research for nuclear weapons effects simulation (NWES) for many years. This research has presented DNA with an opportunity to integrate this electron beam technology into EBDS, to provide an affordable electron beam dry scrubbing of stack gases. Over the past twenty years, EBDS has demonstrated the efficient removal of  $\text{SO}_2$  and  $\text{NO}_x$  from the stack gas of coal-fired facilities and  $\text{NO}_x$  and air toxins from the flue gas of incinerators. The DoD is mandated by the CAAA of 1990 to reduce emissions from its incinerators of  $\text{NO}_x$  and air toxins: these pollutants contribute significantly to the smog problems in urban areas. In addition, coal-fired facilities contribute significantly to acid rain and other air pollution problems through emission of  $\text{SO}_2$  and  $\text{NO}_x$ . This problem is common to DoD coal fired facilities, and many commercial facilities. Furthermore, civilian utilities in the eastern United States which rely on high sulfur coal mined in the Appalachian area will also be severely affected by the CAAA 1990, which mandates significant reduction of both  $\text{SO}_2$  and  $\text{NO}_x$  emission for existing plants and new construction.

Until now conventional electron beam generators have been too expensive for cost effective application of EBDS. However, in support of NWES, the Balanced Technology Initiative (BTI) and the Strategic Defense Initiative Office (SDIO), DNA has developed the high power transformer accelerator (HPTA), electron beam generator. This can satisfy the power, size and cost requirements for an EBDS process affordable by the utilities and DoD boilers burning high sulfur coal and incinerators burning municipal solid waste (MSW)

Specifically, using the HPTA technology, DNA will develop a high power, continuously pulsed electron beam generator; the major elements and support subsystems are:

- (1) Slow power condition system, which includes main power supply, command resonance charge unit and thyatron switched unit;
- (2) Saturable reactor modulator, which includes saturable reactor units, pulse forming lines, output lines, and reset circuits;
- (3) High Power Transformer Accelerator which includes the cells, HPTA support structure, cathode stalk and its support structure;

- (4) Electron Gun (E-Gun) which include thermionic-cathode support structure, thermionic cathode, grids, grid driver, foil and foil support structure;
- (5) Instrumentation Command and Control (IC<sup>2</sup>) which includes all diagnostics, safety interlocks and operation;
- (6) Auxiliaries which include oil, water, and vacuum subsystems; heat exchangers; flowing gas load which includes duct-work, dryers and blowers; and facility modifications such as prime power, conduits, storage tanks and thermal management.

In addition, DNA will derive an optimum layout of an EBDS treatment facility utilizing HPTA for the electron gun.

#### **Expected Payoff:**

The DoD is mandated by the CAAA 1990 to significantly reduce the emissions of air toxins and NO<sub>x</sub> from its incinerators, especially those within high smog urban zones or those that can effect these through air motion. A cost effective EBDS (made so through the application of DNA's HPTA electron beam generator technology) would simultaneously remove both of these pollutants. Furthermore, there is now a unique opportunity to transfer defense technologies conceived for use in SDI, BIT, and NWES to the civilian economy to address severe national environmental and economic concerns. With EBDS, a critical national environmental goal mandated by the CAAA 1990 can be met without a devastating economic impact on the coal industry and the users of high sulfur coal. The Defense Nuclear Agency believes that this transfer of defense technology is a very valuable addition to the overall Strategic Environmental Research and Development Program.

In addition, the advent of low cost gun technology will allow the cost effective application of eSCRUB up to 28 DoD coal fired facilities (in the range 10 to 45 MWe), removing ~95 percent of total SO<sub>2</sub> and >70 percent of total NO<sub>x</sub> from each plant. This represents ~47 percent reduction of the total emissions by treating just 21 percent of the total (131) DoD coal fired facilities.

Finally, the development of a compact, high power, high efficiency, continuously-pulsed power system will facilitate a wide spectrum of advanced weapon system developments such as:

- (1) Electronic jamming systems
- (2) Electronic mine clearing devices
- (3) Directed energy weapons such as high energy lasers and high power microwave sources

#### **Transition Plan:**

The Defense Nuclear Agency will collaborate with the Karlsruhe Nuclear Research Center (KFK), which has an active program in the EBDS program with KFK. Karlsruhe Nuclear Research Center will apply the two-step irradiation process and moving gravel bed filter developed by KFK to the high sulfur content coal and moderate de-NO<sub>x</sub> (70 to 80 percent removal efficiency) conditions appropriate to the East Coast of the United States. In addition they will apply the EBDS process to the high deNO<sub>x</sub> and deSO<sub>x</sub>, low deSO<sub>x</sub> and high HCL

levels typical of DoD incinerators burning municipal solid waste (MSP). The Defense Nuclear Agency will also collaborate with the University of West Virginia, which has an active program in the clean coal technology. They will assist in the analysis of EBDS for incinerators and utilities, along economic analysis of the by-product (fertilizer) value.

During FY 92, DNA will perform an integrated test of these HPTA subsystems:

Average Power	0.5 MW
Run Time	10 Minutes
Beam Kinetic Energy	800 keV
Beam Current	6 kA
Load	Flowing Gas

Also during FY 92, DNA will task KFK to document EBDS under conditions simulating high sulfur east coast coal and DoD incinerators burning municipal solid waste. Both the KFK II AGATE II Test Facility and kinetic reaction computer models will be applied.

**Funding: (\$K)**

<b>FY92</b>	<b>FY93</b>
6000	833

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## **SERDP Thrust Area: Compliance**

**Title:** Shipboard Non-oily Wastewater Treatment System

### **Problem Statement:**

This project will develop and demonstrate membrane-based graywater and blackwater treatment technology for forward fit into surface ships of the year 2000, providing ships with the capability to operate in environmentally sensitive areas by: (1) meeting future national and international water quality standards, and (2) meeting the requirements of DoD Directive 6050.4. This program significantly enhances and expands upon an existing Navy program whose major objectives are to minimize blackwater generation rates by vacuum-collecting water closet and urinal wastes and minimize graywater generation through process changes and reduced flow plumbing fixtures.

The crew and passengers aboard commercial and military ships generate large quantities of blackwater and graywater (30 to 45 gallons per person per day yields 7500 to 11,250 gallons per day from a destroyer; 180,000 to 270,000 gallons per day from an aircraft carrier). Blackwater is from urinals and water closets. Graywater is from shower, laundry, lavatory, scullery and galley. Current provisions of the Clean Water Act (CWA) control the overboard discharge of untreated blackwater within the contiguous zone of the United States, and implementation of Annex IV of the MARPOL Protocol (The International Convention for the Prevention of Pollution from Ships) will regulate the discharge of blackwater from all ocean-going ships world-wide. The Navy anticipates that graywater discharges will be similarly regulated in the near future. No proven wastewater treatment technology exists today that will reliably meet both the effluent quality requirements of MARPOL Annex IV and the operating requirements of ocean-going ships (highly reliable, maintainable, supportable, and safe).

U.S. Navy ships today collect and hold only blackwater in collection, holding, and transfer (CHT) tanks for up to 12 hours, or until tank capacity is reached, while transiting the U.S. 3-mile contiguous zone. Graywater is discharged directly overboard. In the future, the 3 mile limit will probably be extended to 12 miles and graywater discharges will also be regulated. Other nations visited by U.S. naval and commercial ships are also expected to impose more strict environmental laws as well. Ships that rely on holding tanks will be not be able to comply.

### **Project Description:**

The technical objective of this project is to demonstrate ultrafiltration membranes as the basis for a treatment process for shipboard graywater, blackwater, and combined graywater and blackwater aboard a U.S. Navy auxiliary ship (submarine or destroyer tender). The successful shipboard system will be capable of consistently producing an effluent that meets water quality standards of 30 mg/l for Biochemical Oxygen Demand (BOD), 30 mg/l for Total Suspended Solids (TSS), fewer than 14 Fecal Coliform/100 ml, and be non-toxic.

Ultrafiltration membranes have been used by industry to treat water and wastewaters for several decades. New materials and innovative geometries have improved membrane

reliability and increased permeate rates while reducing size requirements. These new membrane materials and systems have successfully treated shipboard oily wastewaters in laboratory and field evaluations. Application to shipboard non-oily wastewaters is promising.

The approach will be to conduct laboratory evaluations of selected commercially available systems, membranes, and technologies and determine their ability to process blackwater, graywater, and combinations of the two. The most successful candidate(s) will be incorporated into a full scale prototype and installed on a Navy vessel for evaluation and demonstration. Cost/benefit analyses and safety studies will be performed. Evaluation and demonstration results will be transitioned to the Naval Sea Systems Command's Shipboard Environmental Protection Program (NAVSEA 05V) for inclusion in the Shipboard Systems Acquisition Program. This project will consist of the three major tasks listed below.

- I. Evaluate candidate membranes, systems and process in the laboratory.
- II. Design and fabricate shipboard prototype non-oily waste water treatment system.
- III. Install prototype aboard Navy test ship, operate and evaluate membrane performance, life expectancy, and cleaning requirements.

This project supports the Department of Defense objectives of environmental compliance and unrestricted access by DoD vessels to all navigable waters and ports worldwide.

The Navy has just begun a very limited technology evaluation of membranes for treating shipboard graywater and oily bilgewater. That program has identified ultrafiltration membranes as the most promising approach.

The major technical risks in pursuing this program are the shipboard interface requirements for space, weight, energy, operator attention, and maintenance. Two important maintenance items will be membrane life expectancy and membrane cleaning requirements.

#### **Expected Payoff:**

Successful development ensures compliance of every DoD vessel with all current and anticipated graywater and blackwater discharge regulations. Ships could then operate in restricted zones, ports, and harbors for extended periods of time and avoid the costs associated with non-compliance violations. Additionally, the cost of discharging non-oily wastewater to port handling facilities could be avoided; the Navy has spent 5 million dollars annually for this purpose in Mediterranean ports alone.

The result of this program will be a shipboard non-oily wastewater treatment system. The system will be applicable to U.S. Navy ships, U.S. Army ships, commercial vessels, off-shore platforms, and possibly as a mobile waste treatment plant for Army and Marine ground operations. Finally, the potential for recycling treated effluent will provide a beneficial impact on energy needs to produce fresh water and for areas of the world with severe water shortages.

## Milestones:

During the FY93 execution year the following will be accomplished:

1. Identification of promising membrane configurations.
2. Evaluation of membrane performance for Graywater, Blackwater, and Combined wastewater in the laboratory.
3. Assessment of pre/post filtration/treatment requirements.
4. Preliminary membrane cleaning tests.

During the FY94 execution year the following will be accomplished:

1. Award contract
2. Evaluate membrane treatability
3. Assess pre/post treatment requirements
4. Conduct membrane cleaning and longevity tests
5. Determine ship interface requirements

During the FY95 execution year the following will be accomplished:

1. Identify membranes, systems, geometries, and materials
2. Prepare conceptual shipboard designs for 300 man ship
3. Design shipboard prototype
4. Conduct preliminary hazard analysis
5. Select test ship
6. Fabricate prototype
7. Prepare installation drawings
8. Install aboard test ship

During the FY96 execution year the following will be accomplished:

1. Prepare preliminary O&M manual
2. Conduct ship evaluation/demonstration
3. Transition to NAUSEA Advanced Development/Acquisition Program

## Transition Plan:

Upon completion of this project in FY96, the product will be transitioned to the Naval Sea Systems Command (NAVSEA 05V). The transition roadmap will be as follows:

FY93-FY96 ==>>	FY97-FY99 ==>>	FY00+
SERDP Execution	Develop final software documentation, level III drawings, specifications, Preproduction Prototypes fabrication, Shock/Vibe/EMI testing, TECHEVAL/OPEVAL/AFP	Procure/Install the equipment fleetwide

The NAVSEA program manager (SEA 05V) will direct this development under SERDP in order to ensure that the product will meet the fleet's needs. Since commercially available membranes will be used, industry will be able to meet the production requirements.

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
1325	1325

**Performer:**

Department of the Navy  
Carderock Division, Naval Surface Warfare Center  
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The U.S. Navy is the lead agency for Global Marine Compliance under the DoD Environmental Quality Strategic Research and Development Plan. All environmental research by the Army, Navy, and Air Force is coordinated through this Reliance plan. Additional Coordination of this project is envisioned between U.S. Navy, U.S. Department of Transportation (U.S. Coast Guard), U.S. Environmental Protection Agency, and the U.S. Army (Belvoir RD&E Center). Membrane and membrane system manufacturers will be involved in the design, testing, and fabrication of laboratory and shipboard prototype test systems.

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## **SERDP Thrust Area: Compliance**

**Title:** Single Event Noise/High-Energy Impulsive Sounds and Human Response Prediction Model Development

### **Problem Statement:**

The National Environmental Policy Act (NEPA) requires the U.S. Air Force (USAF), and the other DoD components, to predict the effects on the environment of all major proposed changes in aircraft operations. Community annoyance in response to aircraft overflight noise is one of the most significant environmental effects addressed in environmental impact analyses documents. As part of the evolution of an acceptable methodology to predict community annoyance in response to aircraft overflight noise, the Environmental Protection Agency (EPA), the National Park Service (NPS) and concerned citizen groups who have participated in public scoping meetings have increasingly requested that the USAF address human annoyance due to individual aircraft overflights. Furthermore, research by the Army on artillery fire found higher annoyance responses at sound levels much lower than a sonic boom. The Army has continued to study artillery fire and blast noise compared to helicopter and wheeled vehicle transportation noise.

The recent report of the Federal Interagency Committee on Noise (FICON) (1992) stated that single event impact analyses should be considered for inclusion in environmental impact analyses under certain circumstances. Additionally, the Congressionally-mandated Department of the Interior NPS Wilderness Overflight study is exploring the use of single event annoyance analysis, using a technical approach similar to that being considered for the present project, for determining acceptable noise levels from military flight operations over NPS lands. The modeling capability proposed for development is especially critical in order to be prepared to respond technically to expected Congressionally mandated noise restrictions (which may vary from no overflights of these areas to severe noise exposure budgets) over national parks and Wilderness areas.

The goal of this project is to address the concerns of various federal agencies and citizen groups interested in environmental noise assessments by developing a single event noise exposure/high-energy impulsive noise and community response prediction model. Additionally, the new project would conduct studies to provide definitive and technically defensible data to avoid future controversies and long delays in the EIS approval process under NEPA.

### **Project Description:**

The technical objective of this project is to develop a scientifically valid methodology for predicting noise exposure levels and human responses to individual aircraft overflight events. It will also conduct human and community response studies of different types of high-energy impulsive noise (sonic booms, blast noise and artillery fire, as well as noise created by aircraft overflight). The single event dosage-response model will be used to perform environmental impact assessments of planned operations for both airbases and rural environments (i.e., MTRs, MOAs, weapons ranges). Planned overflights of U.S. Forest Service and National Park Service lands will, however, be the primary focus for the application of the model being

developed. Techniques for generating an orthographic projection of noise exposures in complex terrain using Geographic Information System (GIS) technology will be explored.

The technical approach will build on the results of related, already completed projects and will be technically comparable to the methodology currently in use for predicting cumulative community noise exposure and annoyance. The resulting computer model will be used by environmental planners as one tool for planning future operations and assessing the environmental impacts of these planned operations on exposed populations. This proposal is divided into two major tasks:

#### Task 1: Development of Single Noise Exposure and Human Response Prediction Model

##### Subtask 1 - Technology Assessment

- (1) Acquire models, etc. used by other DoD related projects.
- (2) Compare viability of alternative technical modeling approaches.
- (3) Choose best modeling approach.
- (4) Address noise metrics issues (SEL, Lmax, peak sound level, etc.).

##### Subtask 2 - Development of Prototype Single Event Noise Exposure and Human Annoyance Prediction Model

- (1) Develop prototype single event noise-annoyance prediction model.

##### Subtask 3 - Acquisition of Single Event Human Annoyance Data

- (1) Conduct laboratory and field single event human response studies.
- (2) Resolve human response metrics issues (e.g., annoyance versus detectability).

##### Subtask 4 - Development and Validation of Final Model

- (1) Develop final model.
- (2) Conduct field model validation tests including tests in low ambient noise environments.

#### Task 2: Annoyance Response to High-Energy Impulsive Sounds

Subtask 1 - Paper study to combine different human-response studies of impulsive noise to derive a dose-response.

Subtask 2 - Lab study to develop a dose-response type of relationship for impulsive and non-impulsive noise.

Subtask 3 - Lab study to compare annoyance response to different types of impulsive noise.

Subtask 4 - Field study to validate the models derived from the lab experiments by exposing panels of human subjects in a real-life home setting to actual sonic booms and noise from large weapons firing.

**Expected Payoff:**

The Air Force will produce Environmental Impact Analysis Process (EIAP) documents that are more scientifically and politically acceptable to Congress and the public by having a validated noise-annoyance (impact) analysis model. This model will improve the ability to accurately predict noise propagated under complex terrains and atmospheric conditions. This capability will complement existing cumulative exposure noise prediction models, particularly in the diverse rural environments where most operational training occurs.

**Milestones:**

FY93

Evaluate hardware and software of existing modeling approaches being explored by other DoD organizations and agencies. Conduct literature review on attitudinal response to noise.

FY94

Conduct two lab studies, choose optimal modeling approach and develop prototype models.

FY95

Determine human annoyance response to noise exposure from individual aircraft overflight events. Conduct field tests.

FY97

Develop final version of single event noise-annoyance model and conduct field validation studies.

**Transition Plan:**

The single event noise exposure and human response model resulting from this project will be transitioned through the Air Force Center for Environmental Excellence to the environmental planning community either as a stand-alone model or by incorporation in the Assessment System for Aircraft Noise (ASAN) being used for aircraft noise related impact assessments for Military Training Routes and Military Operating Areas.

The new-dose-response relationship would be implemented in current models/assessment methodologies used by DoD for assessing the environmental impact of high-energy impulsive noise.

**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
Task 1	150	300
Task 2	200	300
Total	350	600

**Performers:**

Air Force - Armstrong Laboratory (AL/OEBN)

Army Civil Engineering Research Laboratory (CECER/EN)

Research contractor (e.g., BBN Systems and Technologies, Inc., Spectrum Sciences, Inc., Wyle Laboratories)

Coordination: National Park Service Wilderness Overflight Study, Army Construction Engineering Research Laboratory, Academia (e.g. Penn State Univ, Univ of Mississippi, Stanford Univ, Univ of Utah)

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## **SERDP Trust Area: Compliance**

**Title:** Turbulent Boundary Layer Effects on Sound Propagation

### **Problem Statement:**

The objective of this research is to identify the key atmospheric mechanisms that influence sound propagation into communities.

The atmospheric boundary layer is the most rapidly changing portion of the atmosphere. It has the most important short-term influence on waves propagating above the earth's surface. Striations within the boundary layer contribute to ducted propagation near the surface or form acoustic shadow zones. Predictions of the sound field at large distances (greater than 1 km) from noise sources cannot be made based on the average ambient atmospheric properties alone; the theory must include and account for atmospheric turbulence.

Previous work has pointed to atmospheric turbulence. But we have as yet only a qualitative description for some of these effects.

### **Project Description:**

Scattering of waves by turbulent media has been studied thoroughly for many media; but has not been adequately explored for sound waves outdoors. The fundamental mechanism is still not known. Scattering of sound into shadow zones is routinely verified by experiment, but the precise scattering mechanism has not been determined. Two strong candidates are large-scale wind-driven turbulence or small-scale fluctuations in refractive index.

The measurements that must be made require high speed analyzers and digital signal techniques that are very new, but widely known. The important statistics, and correlate them with the atmospheric dynamics. The hypothesis of large-scale turbulence will be tested by perturbing the atmospheric profiles in sound propagation calculations. The Fast Field Program, modified for use with piece-wise linear sound speed profiles, will be used to examine the sound levels due to refraction alone. The parabolic equation method will be used to study the field due to small-scale, range-dependent turbulence. For both types of propagation simulations, further predictions of the longitudinal and transverse spatial and temporal coherence will be made and compared with new experimental measurements.

### **Expected Payoffs:**

Results from this study will be used in computer programs for predicting noise levels and in constructing noise contours. These programs, NOISEMAP and BNOISE, are used by the Army Environmental Hygiene Agency to map noise contours for army installations. Other agencies are in need of this information; for example, the results should yield many important applications in environmental noise prediction, acoustic surveillance and detection, particularly in the tank and helicopter detection and countermeasures. Specifically, the Navy is concerned about noise from naval air stations and firing ranges like Bloodsworth Island in the Chesapeake Bay and Kohoolawe Island in the Hawaiian Islands because of the unique aspects of sound propagation over water. This is important United States research input to

NATO/CCMS.

**Milestones:**

Use perturbations of measured profiles with the FFP	FY93
Study short range, range dependent media with the PE	FY93
Develop boundary conditions for waves in random media	FY94
Model and measure spatial and temporal coherence	FY95
Extend coherence predictions to level fluctuation model	FY96

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
175	225

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## **SERDP Thrust Area: Compliance**

**Title:** Small Arms Range Noise Mitigation Technology Demonstration

### **Problem Statement:**

The goal of this project is to demonstrate, and disseminate knowledge of, recently developed advances in cost effective strategies and techniques for reducing community noise disturbance due to the firing of rifles, shotguns and pistols at small arms ranges.

Because of noise, the DoD has lost significant mission capability at over 50 installations. A very large number of small arms ranges are under increasing pressure to reduce noise output or cease operation, a result of increasing population encroachment and increasing public concern with environmental quality. Small arms (rifles, pistols and shotguns) are fired extensively at ranges for purposes of military and law enforcement training and for recreational and competitive shooting. The noise of such firing can disturb people living in the surrounding community, which can lead to noise complaints and attempts to curtail the firing activity, including political (including congressional) pressure and legal action. Loss of such ranges severely compromises the capability of military and law enforcement organizations to carry out their mission. The recently developed small arms range noise mitigation guidance needs to be conclusively demonstrated in a realistic operational range scenario.

USACERL has carried out a series of exploratory development projects aimed toward mitigation of small arms noise. Accomplishments have included evaluation of and development and testing of design algorithms for: interlane noise shields; noise barrier walls for the rear and sides of ranges; firing sheds (roofed partial enclosures of the firing line); analysis of a very costly German coffered ceiling range design; the detailed effect of ground absorption, ground reflection and atmospheric absorption on small arms noise; and utilization of existing terrain features. Basic research investigations of propagation and terrain effects have also contributed to small arms mitigation techniques. A Navy study of far field noise contours and acoustic directivity of guns provides considerable information regarding guns as acoustic sources.

### **Project Description:**

The technical objective of this project is to demonstrate that recently developed noise mitigation techniques can reduce small arms range noise by at least 10 dB. This is a significant noise reduction that amounts to a halving of subjective noise annoyance. This can easily result in reclassification of the range noise impact into the next lower ICUZ/AICUZ land use compatibility category. The approach will be to upgrade an existing small arms range to achieve lower community noise levels. Upgrades may include designing and constructing some combination of interlane shields, noise barrier walls, and utilization of existing terrain.

Tasks for this project include:

Choose candidate sites

Feb-May93

Analyze each site, choose optimum demo site	May-Jun93
Range noise mitigation acoustical design	Jun-Sep93
Structural design and construction contrast	Sep93-Jun94
Construction	Jun94-Feb95
Test and evaluate	Feb95-Jun95
Prepare design guide for users	Jun95-Sep95

Lack of demonstrated noise mitigation technology greatly hinders execution of the AICUZ/ICUZ noise management process and the EA/EIS process. The DoD cannot fulfil its noise compatibility planning process as required for example by AR 200-1 Chapter 7 when it lacks the demonstrated methodology to design small arms ranges to comply with land use compatibility noise zones. The DoD fails to comply with NEPA when it ignores proper assessment and mitigation of noise from small arms ranges. The DoD is not in compliance with noise laws and regulations in many states.

This project is part of the EQ Reliance Strategy Plan. There is no other past or planned project for demonstration of inexpensive small arms range noise mitigation techniques.

The technical risk of unsuccessful demonstration of the stated noise reduction objective is small. The greater risk is that the noise mitigation techniques will not be used if they have not been demonstrated to be effective in realistic scenarios. This can result in loss of training capability and operational effectiveness which could otherwise have been retained.

#### **Expected Payoff:**

This technology is immediately applicable by, and is needed by, all of the elements of the DoD, since all of them carry out small arms training and practice programs. These include the Army, Navy, Air Force, Coast Guard, USMC, and National Guard and Reserve units. The technology is of special OCONUS utility since crowded conditions and limited real estate often dictate that small arms ranges be located close to dwellings. The technology will also have wide applicability to law enforcement and private and municipal recreational small arms ranges, which are often located in noise sensitive settings.

Incorporation of noise reduction techniques in the design of a small arms range, either during original design (the best option) or as retrofit, is very cost-effective. The cost of noise reduction can add tens to hundreds of thousands of dollars to the cost of a range, depending on size, design and state of repair. The alternative is often relocating the range, which is almost always much more expensive, usually measured in millions of dollars. Another benefit/cost issue is avoidance of costs associated with encroachment and compatible land use. The Navy has spent over \$500 M in land purchases through the AICUZ program because of encroachment. A conservative estimate of off-post noise sensitive encroachment growth is 3 acres per day, DoD wide in Zone II and 0.03 acres per day in Zone III. Conservative estimates of noise-related property devaluation because of noise is 10 % in Zone II and 50 % in Zone III. Noise sensitive property (e.g. new housing) is valued at \$500 K per acre, so the future cost is on the order of \$157 K per day (10% of [3 x 500 K] plus 50% of [0.03 x 500 K]). A cost of \$157 K per day has a present value of about \$ 750 M at a 7.5% interest rate. Proven noise mitigation techniques are needed to avoid these costs. Additional benefit will accrue because of maintained mission capability.

**Milestones:**

Choose candidate sites	May93
Choose optimum demo site	Jun93
Complete acoustical design of noise mitigation measures	Sep93
Structural design and construction contract awarded	Jun94
Structural design and construction completed	Feb95
Test and evaluation completed	Jun95
Design Guide	Sep95

**Transition Plan:**

This project will require coordination with the Army, Navy, Air Force, Coast Guard, USMC, National Guard and Reserve units, and law enforcement agencies. Close liaison will be maintained with the Army Environmental Hygiene Agency, which is the technology transfer agent for noise mitigation technology for the Army and deals with a wide range of users of noise mitigation technology.

**Funding: (\$K)**

FY93  
100

Choose candidate sites	20K FY93
Analyze each site, choose optimum demo site	30K FY93
Range noise mitigation acoustical design	50K FY93
Structural design and construction contract (USACE)	375K FY94
Test and evaluate	50K FY95
Prepare design guide for users	100K FY95

**Performers:**

The project will be carried out by the U.S. Army Construction Engineering Research Laboratory, Champaign, IL, with assistance in construction of needed facilities by the U.S. Army Corps of Engineers. No industry involvement or cooperative development agreements are anticipated.

**Technical Point of Contact:**

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## **SERDP Thrust Area: Compliance**

**Title:** Contaminant Dispersal Model for San Diego Bay

### **Problem Statement:**

The goal of this proposal is to incorporate a contaminant dispersal and fate model into an ongoing environmental risk assessment of Navy contaminants in San Diego Bay, CA. This effort can serve as a prototype for other Navy harbors.

The Navy evaluates the environmental impact of past, current, and proposed operations in order to conform to federal, state, and local law. Environmental risk assessment is the favored approach for detailed studies. Models of contaminant dispersal, in addition to measurements of contaminant release and toxicity, are central to assessing contaminant impact to the environment. Models predict expected concentrations and fate of contaminants, allow for better sampling design to validate predictions, and can be used to predict effects of proposed or alternative operations.

The Environmental Sciences Division at NRD has begun a three to four year environmental risk assessment [fuel oils (primarily aromatic hydrocarbons), copper and other contaminants] released by the Navy into San Diego Bay. The purpose of the assessment is to determine both the absolute impact of Navy releases, as well as the relative impact compared to other, non-Navy sources. These programs are funded by the Naval Facilities Engineering Command and Naval Sea Systems Command with related projects funded by NAVSEA and OCNR. We propose to augment this program with a new modeling approach and computer visualization which are beyond our current capabilities and budget. This enhancement will provide significantly more power to the predictive capabilities of existing models.

### **Project Description:**

The Environmental Protection Agency has been the chief author of contaminant disposal and fate models for the past two decades. An EPA hydrodynamic model DYNHYD has been tailored to the bathymetry of San Diego Bay and efforts are currently underway to validate predictions with field data. DYNHYD is quasi, two-dimensional model with low spatial resolution (140 node). To supplement DYNHYD, Dr. R. Cheng at the U.S. Geological Survey in Menlo Park is assisting in the application of a high resolution (130,000 node), finite difference model to San Diego Bay. Previous and current work also includes mapping the distribution and flux rates of aromatic hydrocarbons and free ionic copper in the water column and sediments from our survey craft. In addition, we have completed installation of a bioassay laboratory in which to test contaminant toxicity on common and EPA-standard marine organisms. Some of this work is the result of ongoing, Navy-funded projects.

We propose to develop a modeling framework that includes water, sediment bed evolution, and contaminant transport and fate in San Diego Bay. The models will be developed by the Army Corps of Engineers Waterways Experimental Station (WES) and incorporated into the risk assessment program. The WES model uses a different computational approach, the accuracy of which we can compare to the EPA's and Cheng's model; it has two and three dimensional capabilities and flexible grid resolution, and will be able to predict the

partitioning and degradation of contaminants. Field data and model results will be expressed simply and graphically.

The WES models will be developed, calibrated, and verified at the Army laboratory in Vicksburg, MS. Hydrodynamic validation in San Diego Bay will be made with an acoustic doppler current meter mounted on our survey craft, which provides real-time current data. Contaminant predictions will be validated by real time hydrocarbon and copper sensors on the same vessel, and from discrete samples taken for laboratory analysis.

This proposal supports Global Marine Compliance objectives to develop cost effective monitoring/risk assessment approaches for prediction of environmental impact of shipboard and related systems. It further enhances our ability to conduct environmental risk assessments by providing powerful, predictive models of contaminant dispersal and fate. From such data, we can define the biological impact of past, present and proposed Navy operations in San Diego Bay.

Much of the data being collected in San Diego Bay, to be used in this study, come from projects previously funded by the Navy. These include examination of the impact of underwater hull cleaning, fuel spills, storm water runoff around Navy installations, and development of novel bioassays. We are coordinating our proposed work and data collection with NOAA, which plans to make an EMAP-type toxicity and sediment chemistry survey of San Diego Bay, and with California's Fish and Game Department and California State University at Long Beach, which are designing in situ mussel toxicity studies. The work we propose in cooperation with WES is consonant with their interests in expanding the use and validation of contaminant models.

The Tasks for accomplishing this projects successfully are outlined below:

1. Data acquisition: The Navy will provide data for boundary model conditions, initial conditions, calibration and verification. In addition to data collected under other Navy and NOAA programs, the modeling effort will require collection of site-specific sediment characterization data.
2. Hydrodynamic model: Development of the three dimensional hydrodynamic model of San Diego Bay will include all major forcings, such as tide, wind, and density effects that impact the three-dimensional circulation. Important processes, such as vertical turbulence mixing, wind driven circulation, and spring-neap tidal effects will be considered. Linkage with the sediment model will require modification of an existing numerical model. Extensive testing of numerical grids with varying resolution will be required to ensure proper linkage. Validation of the hydrodynamic model will be accomplished using Navy Acoustic current meter and tidal height data covering a wide range of commonly occurring events. Production runs of up to five years will be made to provide flow fields for the long-term simulations with sediment transport and contaminant models.
3. Sediment transport model: Suspended and bedload transport will be modeled over a grid which can be either two or three dimensional. An unlimited number of sediment size fractions will be treated. Sediment calculations will be coupled to hydrodynamic calculations allowing feedback between the flow field, bed evolution, and bed-surface size distribution.

The model will first be developed for coarse-grained, cohesion-less sediments (silts, sands, and gravels), then demonstrated on a bend of the Mississippi River. Cohesive sediment fractions will then be added allowing for winnowing/armoring of fine-grained sediment, binding of coarse-grained sediments by cohesives, and variable erodibility as conditions dictate.

4. Contaminant transport model: The technical approach will involve four steps: development, interfacing/adaption, calibration, and validation of the contaminant transport and fate model. Contaminant modeling modules will be incorporated into CE-QUAL-ICM (the Corps of Engineers three-dimensional water quality model) resulting in a state-of-the-art and contaminant model. The contaminant model will be interfaced to the existing CE-QUAL-ICM water quality model. This model system will then be interfaced to the selected three-dimensional hydrodynamic model, which must include sediment transport. The sediment transport model is required to provide the proper information for suspended solids dynamics, which play a major role in contaminant transport. The modelling system will be calibrated and validated against water quality and contaminant data collected in San Diego Bay. The model must be capable of making reasonable predictions of contaminant concentrations over the past decade.

5. Visualization: Visualization tools developed at WES will be adapted to the San Diego Bay application. These tools will be made available to Nrad for incorporation into a user-friendly environmental modeling and visualization package. This package will serve as a prototype for other Navy harbors and estuaries.

This modeling effort will require two phases of model development: (1) an interface between the sediment transport model and the contaminant transport model, and (2) a model for contaminant transport and fate. The sediment bed and transport submodel which calculates sediment concentration in the water column, contaminant concentrations in the bed, and sediment entrainment and deposition at the bottom is essential to describe contaminant transport. Contaminants are normally attached to fine grain sediments and thus the sediment bed is the major long term source/sink of contaminants in a water body. Sediment resuspension by propeller wash and subsequent transport by currents regularly occurs and must be addressed. One of the difficult issues is the construction and validation of model contaminant partitioning. We have several factors in our favor, however, which make this feasible:

(1) The contaminant sources are well defined, easy to reach, and have been measured extensively in the past by NRaD surveys.

(2) From a hydrodynamic point of view, San Diego Bay is an ideal test ground for the model in that it has only one entrance, has little fresh water input, is unstratified, and is small enough to map with our survey craft.

(3) Our survey craft has extensive measurement capability. Since many pertinent measurements can be made continuously and displayed in real time it is well suited to testing model results. Our sampling position is determined with differential satellite GPS data, allowing easy replication. We have proficiency and the necessary analysis equipment to measure low aromatic and metal concentrations in discrete samples.



### Expected Payoff:

On completion, we plan to make the San Diego Bay model generally available to other users. Several Navy Facilities on San Diego Bay will benefit from risk assessment studies in general and modeling in particular. These facilities often undertake construction or dredging projects, which require study of likely environmental consequences under the National Environmental Policy Act (NEPA, CWA or RCRA). Model predictions could play a key role in such assessments. It is possible that several San Diego naval facilities will be placed on the National Priorities List (Superfund). A developed model could be incorporated directly into the remedial investigation/feasibility study (RI/FS) process, saving time and money. Other potential users include the San Diego Sewage Treatment Plant which is particularly interested in the remedial effects of construction to improve existing treatment facilities, the San Diego Port Authority, and Regional Water Quality Control Board.

Model predictions of contaminant dispersal allows: determination of the absolute and relative impacts of multiple contaminant sources; anticipate environmental impact of proposed activities; more efficiently designed sample plans.

### Milestones:

Projected accomplishments in first year:

- a. completion of the WES hydrodynamic model and start of the contaminant transport code.
- b. validation and accuracy comparison of WES and Cheng's hydrodynamic models
- c. measurement of water and sediment concentrations of aromatic hydrocarbons and copper in the vicinity of the Naval Station
- d. measurement of input rates of aromatic hydrocarbons (from fueling spills, storm water runoff, floating oil/water separators, creosote-soaked pier pilings, sediment), and input rates of copper (from storm water runoff, Navy in-water hull cleaning, sediment)

Milestones over project lifetime:

	FY93	FY94	FY95	FY96
1. Hydrodynamic validation and comparisons	S-----C			
2. Sediment transport development and validation	S-----C			
3. Develop hydrodynamic/water quality/sediment model interface	S-----C			
4. Contaminant transport development/validation	S-----C			
5. Visualization			S-----C	
6. Technology transfer and training				S---T

### Transition Plan:

Two basic products should come out of this project. The first is an environmental risk assessment of aromatic hydrocarbons and copper entering San Diego Bay in the vicinity of the Naval Station as a result of Navy activities. These contaminants and this site was chosen after consultation with staff at the South West Engineering Field Division, and represents one of the larger Naval environmental problems in San Diego Bay. The second product is a

contaminant dispersal and fate model that has much broader applicability to a larger audience. The primary users will probably be Naval facilities and as the model develops, the "front end" will be tailored to the needs of these and other potential users.

**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
NCCOSC	290	260
ACOE/WES	400	475
TOTAL	690	735

**Performers:**

US Navy: Naval Command Control and Ocean Surveillance Center RDT&E Division  
US Army Corp of Engineers: Waterways Experimental Station  
US Geologic Survey: Water Resources Division

**Technical Point of Contact:**

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## **SERDP Thrust Area: Compliance**

**Title:** Portland-Cement Concrete Liners and Tanks for Isolating Hazardous Wastes

### **Problem Statement:**

The technical goal is to prevent or minimize transport of contaminants out of isolation structures. Many U.S. state and federal agencies now manage sites and materials contaminated by fuels, solvents, radiation, or other chemically toxic substances. One popular approach to remediation and isolation is placement of the contaminated solid or liquid in specially built containment structures. These must be designed with multiple low-permeability barriers or liners to prevent or minimize ingress of groundwater or outward transport of contaminants. Materials used for liners have included plastic membranes, clays, grouts, etc. In addition to having low permeability, structures and liners also must be durable and, therefore, must be resistant to chemical attack from the toxic substances specific to each site. Portland-cement concrete, which is often used as the outer structural layer of such multiple-barrier systems, can be specially formulated to have low permeability and resist chemical attack. Thus, it offers high potential for use as a liner as well as a structural material for waste isolation. This is a new project.

### **Project Description:**

Related studies being conducted at the Waterways Experiment Station involve development of special-purpose cement grouts and concretes for physical and chemical isolation of radioactive and mixed wastes, coordinated with three DOE sites and two U.S. National Laboratories. The WES also is completing extensive research on the relationship between permeability and other concrete durability properties and is evaluating proprietary products designed to enhance durability and permeability of concretes (under the CPAR Program).

The objective of the project proposed herein is to develop criteria for formulation and guidance for use of portland-cement concrete mixtures as containment structures and liners. The technical approach is to conduct a laboratory study to formulate candidate concretes with potential to perform well in difficult service environments and to develop therefrom mixture proportioning and performance criteria and user guidance.

This project is compatible with The Tri-Service S&T Reliance Program Pillar 2, Compliance, Sub thrust 2.L.5: Treatment/Disposal of Operating Installation Hazardous Wastes.

Specific tasks are: (1) define performance requirements in terms of permeability, strength, modulus, chemical resistance, etc.; (2) formulate candidate cement-based mixtures with enhanced properties to meet site requirements; and (3) develop performance criteria (e.g., establish what permeability is good enough) and user guidance.

The most pressing technical issue to be overcome is the negative attitude toward use of concrete and cement in waste isolation, given some recent examples of failures of these technologies at DOE sites where the materials used had not been tailored to the demands of the wastes and the service environment.

**Expected Payoff:**

This technology may be used in the public and private sector alike, by various offices of the DOE, the EPA, their operating contractors, and state environmental departments. It will provide improved, predictable service of conventional and cost-effective materials capability for waste isolation.

**Milestones:**

Milestone 1	Define Performance Requirements	4Q FY 93
Milestone 2	Conduct Laboratory Study	3Q FY 94
Milestone 3	Develop Design Criteria and User Guidance	2Q FY 95

**Transition Plan:**

As candidate demonstration projects are identified and funding is made available, this technology will be transitioned to field application. We anticipate that demonstration projects can be conducted in FY95, FY96, and FY97. This technology can easily be transferred to industry use.

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
90	160

**Performers:**

The primary performer will be the US Army Engineer Waterways Experiment Station. It is possible that future demonstration projects can be performed under Cooperative Research and Development Agreements (CRDA).

**Technical Point of Contact:**

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## **SERDP Thrust Area: Compliance**

**Title:** Capacitive Deionization as a Means of Eliminating Secondary Wastes Associated with Conventional Ion Exchange

### **Problem Statement:**

We propose the development of capacitive deionization as an efficient process for the removal of ionic contaminants from aqueous streams. In this novel process, ions are retained in electric double layers formed at the surfaces of two porous electrodes of opposite polarity. If this process is successful, capacitive deionization will probably replace many existing ion exchange processes, thereby eliminating the associated secondary waste. Such technology could be used to treat various aqueous streams, including waste water, drinking water, boiler water for power plants, and process water for semiconductor manufacturing. Deionization of boiler water is used as a means of preventing fouling and corrosion of heat transfer surfaces. It may even be possible to use capacitive deionization for the energy-efficient desalination of sea water.

Ion exchange is used as a means of removing anions and cations (heavy metals and radioisotopes) from process and waste water throughout the U.S. Department of Energy complex. Such processes generate large volumes of corrosive secondary waste that must be treated. Wastes include used anion and cation exchange resins, as well as contaminated acids and bases. Secondary waste streams due to regeneration of ion exchangers will be eliminated by capacitive deionization. It may also be possible to reduce the amount of  $\text{HNO}_3$  needed for regeneration of cation columns used in processing special nuclear materials. During plutonium processing, resins and solutions of  $\text{HNO}_3$  become contaminated with  $\text{PuO}_2^{++}$  and other radioisotopes. Given the high cost of disposal in mined geological repositories, there is tremendous incentive for reducing the volume of waste that must be dealt with.

### **Project Description:**

In essence, a series of flow-through supercapacitors will be used to remove cations and anions from water. The construction and operation of the device is relatively simple. Two porous electrodes fabricated from carbon aerogel with high specific surface area will be placed in a dielectric vessel and separated by either a cation exchange membrane or a microporous dielectric sheet. Ions will be forced to move to the surfaces of electrodes by an imposed electric field. Cations will concentrate in the electric double layer formed at the surface of cathode, while anions will be concentrate at the surface of anode.

In this case, protons will migrate through the membrane to balance the anodic charge associated with  $\text{Cl}^-$  anions, thereby forming  $\text{HCl}$ . The presence of  $\text{H}^+$  in the cathode compartment may reduce the overall removal efficiency of other cations such as  $\text{Na}^+$ . A microporous dielectric membrane would allow diffusion of both cations and anions and would not allow the formation of  $\text{HCl}$  in the cathode compartment. Separators that allow bipolar transport may be more desirable than the cation exchange membrane.

In addition to process demonstration, development would include the development of computers models that can be used for computational analyses and engineering of large-scale systems. Computer simulations will also be used for parametric optimization. Parameters

that will be determined for a specified separation include: (1) electrode porosity and thickness; (2) separator porosity and thickness; (3) superficial fluid velocity; (3) charging voltage; and (4) number of electrodes (stages). The theory for porous-electrode flow-through capacitors was developed by Prof. John Newman of U.C. Berkeley [J. Electrochem. Soc. Vol. 118, No. 3, 1971, pp. 510-517.].

The effluent from a single capacitive deionizer will be monitored with an on-line conductivity probe, as well as various ion-selective electrodes, and recorded with a strip-chart recorder. An array of sensors can be used to determine selectivities of porous electrodes for various anions and cations in multicomponent electrolytes. Measured effluent concentrations will be compared to predictions for model validation. Practical removal efficiencies will be determined.

Capacitive deionization is a novel and innovative alternative to ion exchange. The electrode material and proposed mode of operation are entirely new. Carbon aerogels have much higher specific surface areas ( $600\text{--}900\text{ m}^2/\text{gm}$ ) than conventional carbon-paste electrodes or activated carbon powders ( $200\text{--}300\text{ m}^2/\text{gm}$ ). By using carbon aerogel as the electrode material instead of carbon paste or powder, the capacity of the deionizer will be increased dramatically (3X). Note that carbon aerogel was developed by Lawrence Livermore National Laboratory (LLNL) and is a "spin-off" of the Strategic Defense Initiative (SDI) Program [R.W. Pekala et al., J. Non-Crystalline Solids, Vol. 145, 1992, pp. 90-98]. Ultimately, the system will consist of two carbon aerogel supercapacitors in parallel (next project year). One capacitor will be regenerated (discharged) while the other purifies (charges). This mode of operation will be called potential-swing ion adsorption and is analogous to pressure-swing gas absorption.

#### **Expected Payoff:**

This new environmental technology will be of value to the private sector. For example, a capacitive deionizer could be used to produce deionized water for use in the boilers of fossil-fueled and nuclear power plants. In the future, it may be possible to use such novel technology for the energy-efficient desalination of water for dry, heavily-populated areas like California. We believe that a bed filled with 2L of carbon aerogel may be able to reduce the NaCl concentration in 55L of water from 1000 ppm to approximately 1 ppm with an energy expenditure of less than 40 Whr. This assumes a polarization of 1.2 V and a surface charge density of  $15\text{ microC}/\text{cm}^2$ . Deionized water, free of dissolved organic resin, could also be used for the manufacture of "next-generation" semiconductors (nanoelectronics). Nano-electronics will be far less tolerant of impurities than microelectronics.

#### **Milestones:**

##### **First Year Activity/Program Plan:**

1st Quarter: a) Development of computational model. b) Design of proof-of-principle capacitive deionization system for batch processing. c) Procurement of vessels, valves, pumps, power supplies, conductivity monitors, ion selective electrodes, and strip-chart recorders. d) Preparation of large quantity of carbon aerogel with high specific surface area.

2nd Quarter: a) Construction of proof-of-principle capacitive deionization system. b) Testing of fluid-flow systems. c) Testing of electrical and electronic systems.

3rd Quarter: a) Measurement of double layer capacitance of carbon aerogel electrodes in various electrolytes at various potentials. b) Measurement of surface charge density of carbon aerogel electrodes in various electrolytes at various potentials.

4th Quarter: a) Measurement of efficiencies for removing simple non-toxic ions from symmetric (z:z) electrolytes. b) Verification and further development of theoretical model. c) Documentation of project.

#### Second Year Activity/Program Plan:

1st Quarter: a) Design of pilot-scale capacitive deionization system for continuous operation. b) Procurement of additional vessels, valves, pumps, power supplies, conductivity monitors, ion selective electrodes, as well as equipment for computer control. c) Preparation of additional carbon aerogel.

2nd Quarter: a) Construction of pilot-scale capacitive deionization system for continuous operation. b) Testing of fluid-flow systems. c) Testing of electrical and control systems.

3rd Quarter: a) Measurement of efficiencies for removing simple non-toxic ions from symmetric electrolytes. b) Demonstration of system with streams of practical importance.

4th Quarter: a) Documentation of project. b) Investigate deployment within DOE and Department of Defense (DoD) facilities. c) Lay work for technology transfer into the private sector.

#### Transition Plan:

The theory for flow-through porous-electrode electrolytic capacitors was developed and published by Prof. John Newman of U.C. Berkeley over 20 years ago (J. electrochem. Soc., 1970). Little or no work has been done in this area since that time. Carbon aerogels with very high surface areas were developed by R.W. Pekala and coworkers at LLNL [J. Non-Crystalline Solids, Vol. 145, 1992, pp. 90-88.]. Dr. S. T. Mayer has developed electrolytic supercapacitors that have carbon aerogel electrodes (aerocapacitors). These new energy storage devices have energy densities of 4-25 Whr/kg, power densities of 0.1-10 kW/kg, and cycle lives greater than 100,000. These and other researchers will be consulted.

#### Funding: (\$K)

	FY93	FY94
Labor	600	923
Supplies/overhead	195	326
Total:	795	1,249

#### Technical Point of Contact:

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## **SERDP Thrust Area: Compliance**

### **Title: Glassy Materials Modeling for Hazardous Waste Immobilization**

#### **Problem Statement:**

The objective of this work is to develop and design vitrification and leaching models for glass materials to be used effectively for immobilization of heavy metal hazardous substances such as lead in paint through in situ vitrification.

Heavy metal hazardous waste residues have been effectively encapsulated in the matrix of glassy materials. The use of a stable glass ceramic class of materials to vitrify, in situ, these residues is currently under investigation. Currently, the actual mechanism by which these materials mitigate hazardous waste has not yet been determined. Preliminary experiments have been used to determine that bonds within the glass network may break, providing bonding sites within this network for the hazardous cations. Similarly the cations may become part of the lattice structure by randomly occupying interstitial and/or defect sites.

#### **Project Description:**

The tetrahedra structure, bond angles, and ionic field strengths of the glass forming and glass modifying oxides will be investigated. One application process, which is under investigation, is to thermally spray a molten glass compound directly onto a lead containing substrate. This has shown the potential to effectively contain the hazardous waste residues. Tests which determine the cation leaching rates, the effect of pH, and the effect of water will be performed on the resultant material to ascertain whether it can be safely disposed of in a landfill. The mechanism by which these waste materials become immobilized will be investigated. This approach will involve the preparation of vitrified materials containing heavy metal hazardous waste and determining through characterization techniques such as X-ray diffraction (XRD), X-ray Spectrometry (XRS), Scanning Electron Microscope (SEM), how the hazardous waste is incorporated within the glass structure and immobilized. The mechanisms of the vitrification and ion leaching processes will be modeled to optimize hazardous waste neutralization by in situ vitrification.

#### **Expected Payoff:**

These include eliminating the environmental and health risks associated with lead and other hazardous wastes.

#### **Milestones:**

Prepare Vitrified Materials	FY93
Lab Study of Varied Processing Parameters	FY94
Investigate Microstructure through Characterization	FY95
Development of Effective Glassy Materials Modeling	FY95



**Funding: (\$K)**

Funding is \$810K for Lead-Based Paint Abatement research on wood and steel substrates.

<b>FY93</b>	<b>FY94</b>
150	250

**Performers:**

University of Illinois is conducting work on glass formation; W.H. Dumbaugh Corning Glass works, NY; J.H. Selverian GTE Laboratories, MA.

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## SERDP Thrust Area: Compliance

### Title: Waste Tank Remediation: Analysis and Waste Form Development: LASER ABLATION-LASER IONIZATION CHARACTERIZATION OF SOLIDS

#### Problem Statement:

The Department of Energy is currently attempting to come to a consensus on the directions to be taken in the enormous task of remediating defense wastes and environmental insults which have occurred over 50 years of weapons production. It is abundantly clear that the technology needed to process and store highly radioactive waste and to remediate contaminated zones does not currently exist. It is also clear that the decision to process DOE's high-level wastes into glass and grout have many technical uncertainties, among which include a general lack of knowledge of the long-term stability and acceptability of these waste forms, the processibility of the tank waste contents, and a consensus on tolerable composition ranges for these wastes.

A major impediment to the development of optimum waste treatment technologies has been inadequate characterization of waste streams. Current characterization, involving hot-cell work on samples removed from tanks, is often both expensive and incomplete. For example, a single analysis of solutions from a waste tank can cost over \$1M. While providing average elemental compositions, the analyses do not identify what chemical compounds, solid phases, or complex species are present. The analyses often fail to detect key species such as  $\text{TcO}^4$ . New analytical techniques and technologies need to be developed, both for more complete and efficient analysis of samples removed from tanks, and for *in situ* analyses using chemical sensors.

The remediation of Hanford-site defense waste and the long-term disposal of high-level mixed wastes requires chemical analysis of the waste streams. Mixed waste analysis is needed to characterize the chemical classes and concentrations of a wide variety of waste materials. Tank and crib waste sites contain enormous distributions of organic compounds; aromatics, nitrates, chelating agents, halogenated hydrocarbons, and inorganic compounds; chromates, ferrocyanides, metals, and TRU's. The speciation and concentration of these materials must be determined in order to design effective remediation strategies. Additionally, the high concentrations of radioactive waste materials, in tanks and cribs, provide an energetic driving force that continuously transforms mixed waste in complex kinetic pathways. A basic understanding of the chemical nature and kinetics of mixed wastes must be obtained prior to initiating safe and effective treatment. We propose to develop widely applicable mass spectrometry techniques for rapid analysis of mixed chemical wastes. Initial research will develop laser based analysis techniques, the principles of which may be extended to field apparatus.

Technetium-99 has been identified as significant ground water contaminant at a number of locations on the Hanford Site. Because of its long half-life (214,000 years), high fission yield, and high rate of mobility in the subsurface, Technetium-99 is considered a hazardous radioisotope waste. Furthermore, Technetium-99 can be used as a critical path isotope for performance assessment of nuclear waste isolation barriers such as the grout vaults in use at Hanford. Because Tc-99 is a long-lived pure  $\beta$ -emitter, routinely available radiochemical-counting methods do not provide adequate sensitivity for use of Tc-99 as a performance assessment tool. However, the long half-life of Tc-99 does make it an ideal case

for high-sensitivity detection by laser resonance ionization methods, which are responsive to the quantity of atoms present rather than the radioactive decay rate. Pioneering work conducted at Johannes Gutenberg Universität Mainz in Germany has demonstrated that multiple-resonance laser induced ionization techniques can be successfully applied to the measurement of Tc-99 in environmental samples. Improvements on this methodology, utilizing newly available, continuous-wave solid state lasers are expected to ultimately result in a field-portable, routine analytical technology capable of rapid, accurate and sensitive measurements.

### **Project Description:**

The major objectives of this research are:

1. To develop general and sensitive techniques for determining the molecular speciation of organics and inorganics in tank wastes and chemisorbed on mineral soil substrates. These methods must be sensitive to a broad spectrum of compounds to detect the many species present in mixed waste environments.
2. To develop new methods for the detection of Technetium. Technetium is difficult to detect with standard counting methods because it is a pure  $\beta$ -emitter. Development of multiphoton-ionization techniques is required to satisfy the critical need for sensitive and rapid detection of Tc-99.

Laser-based analysis techniques are proposed to achieve these objectives, primarily laser ablation mass spectroscopy (LAMS) and resonance enhanced multiple photon ionization (REMPI). Laser ablation can provide gas phase particles from solid samples for analysis by mass spectrometry, laser-induced fluorescence, and other techniques. Analysis of the resulting emissions can be performed rapidly and requires very little sample material. This is highly desirable in the analysis of many environmental samples and hazardous wastes. The LAMS approach couples efficient sample vaporization with ultrasensitive mass spectrometry. Laser ablation can vaporize nearly any solid refractory material in pulsed plumes of sufficient concentration for detailed mass analysis of even complex multicomponent mixtures. When the concentrated laser ablation pulses are combined with multiphoton ionization time-of-flight mass spectroscopy, the result is a versatile and sensitive analysis technique of very high mass resolution. The excellent mass resolution provides superb differentiation between compounds of similar masses and between isotopes. In addition, the resonant ionization process can provide excellent spectral resolution which extends and compliments the mass resolution. These features are crucial for the successful speciation of complex waste samples.

The advantages of the LAMS approach include: small sample requirements, minimum sample preprocessing, minimum waste generation, and reliable technology. However, several uncertainties are introduced by the ablation process. For instance, it is not clear how well the composition of the ablated (gaseous) products reflects the sample composition; some sample components can be preferentially ablated. Changes in the chemical state (e.g., changes in the oxidation state of metals) in the solid and gas phase are also potential problems. We propose to use several concurrent approaches to determine in more detail the mechanisms and consequences of laser ablation on model samples of simulated waste materials, and on relevant wide band gap inorganic materials, with and without chemisorbed species. Of particular importance are the effects of the ablation process, the defect-mediated coupling of light into the solid, the mechanism of particle emission, and particle interactions

after emission but prior to the actual analysis.

The analysis of organic species chemisorbed on mineral substrates is an extremely important application of laser analysis techniques due to the need to detect toxic wastes contained in soils. Many organic molecules absorb strongly in the UV (e.g., trimethylamine, benzene, naphthalene, toluene, phenol, and methyl benzoate) and may prove especially amenable to laser techniques. A thorough understanding of the mechanisms of desorption and ionization of such molecules on macroscopic single crystals of MgO, quartz, and CaCO<sub>3</sub> (which are all transparent down to 200-250 nm) will greatly aid analysis. We will study both neutral and ionic species desorbed from these surfaces, their kinetic energies, and possible electronic excitations (gas phase luminescence studies) as a function of laser fluence and wavelength.

Technetium-99 measurement systems to be addressed by this project will expand upon existing expertise and technology that has been developed at Pacific Northwest laboratory (PNL). Resonance enhanced multiphoton ionization, coupled with mass spectrometry, has been shown to be an extremely sensitive and selective approach to the analysis of rare isotopes. This work at PNL has emphasized the use of high-resolution continuous-wave lasers to simultaneously maximize isotopic selectivity and absolute sensitivity, and has demonstrated detection limits in the attogram ( $10^{-18}$  g) range and the ability to detect a target isotope in the presence of a  $10^{10}$  or greater excess of other isotopes of the same element. Applying these methods to the measurement of Tc-99 will initially involve offsite assignment of B. A. Bushaw at Universität-Mainz to understand the spectroscopy, thermal atomization dynamics, and handling and preparation of environmental technetium samples. Working in collaboration with the researchers at Mainz (and taking advantage of their existing experience) will help determine specific excitation schemes, and we also propose to develop measurement procedures that can be addressed with compact solid state laser systems. Solid state laser technology has the advantages in that it is reliable and easily incorporated into field analytical instrumentation.

#### **Expected Payoffs:**

These programs will increase our capabilities to analyze mixed waste and detect Technetium. The results will be useful in performing the analysis of tank and crib wastes and monitoring tank waste kinetics. The critical task of tank waste analysis must be completed prior to initiating safe and effective waste remediation. The sensitive detection of Technetium-99 will be very useful in tracing this hazardous critical path isotope. All results will be useful in determining the evolution of hazardous wastes in the Hanford environment.

#### **Milestones:**

Work in FY 1993 will focus on laser ablation-laser characterization of solid waste samples and resonant ionization detection of technetium. Initial studies, at PNL, will use laser ablation to vaporize waste compounds deposited on metal surfaces.

1. An ultra high vacuum (UHV) laser ablation mass spectrometry apparatus has been designed and is in construction.
2. A postdoctoral research associate, skilled in UHV and surface science, has been recruited and will begin work in January, 1993. The program plan for the UHV apparatus includes speciation of organic and inorganic waste compounds.

3. A collaboration has been established between Professor Tom Dickinson of the Washington State University Department of Physics and PNL staff in the Chemical Structure and Dynamics program. Professor Dickinson will focus his studies on desorption from wide band gap inorganic materials and metal-oxide substrates. These studies will provide insight into mechanism of molecular desorption from soils.

4. In FY-1993 B. A. Bushaw will begin a half-time offsite appointment at the Universität Mainz in Mainz, Germany. The objective in this year will be to acquire a detailed understanding of the optical spectroscopy of technetium and the application to environmental measurements as developed by the combined efforts of the Institute für Kernchemie and the Institute für Physik at Mainz.

The work in FY 1994 will continue the FY-1993 activities and the information obtained in the earlier studies, of known waste compounds, will be applied to experiments on multicomponent waste compounds.

1. Initial FY-1994 studies will focus on the analysis of nitrates and will be later extended to include organic agents (e.g., EDTA) and inorganic compounds that are important agents in both tank and ground wastes.

2. Studies of mixed wastes to determine multicomponent interferences will be undertaken. Because of the complexity of mixed waste, experiments on multicomponent samples are needed to determine experimental interferences and systematic limitations.

3. The off-site assignment of B.A. Bushaw at Universität-Mainz will continue in 1994. A stabilized, frequency-doubled cw-diode laser system will be constructed for the first-step excitation of technetium. This laser source will be fully characterized and then, in conjunction with the copper-vapor laser (CVL) pumped dye lasers existing at Mainz, will be used to investigate and optimize multiple-resonance excitation schemes for technetium.

In FY95:

1. In FY 1995 LAMS studies will investigate both metal wastes and inorganic chromates and salts. This work could readily be extended to the laser desorption of metallic species chemisorbed on dielectric materials. This is relevant to the monitoring and clean-up of toxic metallic atoms/ions in soil.

2. We will investigate the effect of hydrated surface layers and adsorbed water on the ablation process. Adsorbed water is an important feature of many environmental systems and has profound effects on the surface chemistry of many materials, including the alkali halides and silicate glasses.

3. Technetium detection will be extended to produce a fully defined and optimized excitation scheme that uses wavelengths for which the CVL dye lasers, used in these spectroscopic studies, may be replaced with solid state cw lasers in a prototype analytical instrument.

#### **Performers:**

The proposed work will compliment several other DOE-funded projects including: the Mobile

Analytical Reconnaissance System (MARS), Materials Sciences programs studying chemical sensors and Chemical Structure and Dynamics programs studying laser ablation, resonant ionization and desorption processes from surfaces. The above programs involve collaborations with the Applied Physics Center and within the Molecular Science Research Center (MSRC). A major goal of the MARS program is to develop a mobile system for analysis of tank and crib waste at remote on-site locations. Laboratory studies of the basic ablation process will aid in optimal design of the MARS prototype and are required to calibrate MARS analytical results.

Technetium-99 measurement systems will expand upon existing expertise and technology that has been developed at Pacific Northwest laboratory (PNL). Resonance enhanced multiphoton ionization, coupled with mass spectrometry, has been shown to be an extremely sensitive and selective approach to the analysis of rare isotopes. This work at PNL has emphasized the use of high-resolution continuous-wave lasers to simultaneously maximize isotopic selectivity and absolute sensitivity, and has demonstrated detection limits in the attogram ( $10^{-18}$  g) range and the ability to detect a target isotope in the presence of a  $10^{10}$  or greater excess of other isotopes of the same element. The collaboration of B. A. Bushaw with the Universität-Mainz provides the opportunity to develop and import an essential new technology.

**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
1 FTE Scientist/Engineer (WP Hess); 1 postdoctoral fellow; subcontracts; supplies	217	380
Laser ablation source laser		30
<b>TOTAL</b>	<b>217</b>	<b>410</b>

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## **SERDP Thrust Area: Compliance**

**Title:** Technical and Economic Assessment of Storage of Industrial Waste on Abyssal Plains

### **Problem Statement:**

The technical goal is to assess the concept of storing industrial waste (sewage sludge, fly ash from incinerators, and dredge spoil) in abyssal plains of the ocean floor identifying the advantages, disadvantages, and economic and environmental viability.

- (1) Select typical abyssal plain areas in the North Atlantic, North Pacific and Gulf of Mexico possessing environmental characteristics (geological, chemical, biological and physical) which enable assessments of suitability for abyssal plain waste storage.
- (2) Prepare, for such areas, concepts for planning both site surveys and long-term monitoring.
- (3) Assess candidate methods for waste preparation, dockside staging of waste material, transporting and deep ocean emplacement for technological feasibility and reliability.
- (4) Assess the economic viability of storing industrial waste on the abyssal plains in the deep ocean including the cost factors for site preparation, methodology for staging, transporting and emplacement of industrial waste, and site monitoring.

The disposal of industrial waste (sewage sludge, fly ash from incinerators and dredge spoil) has become one of the most critical problems facing this nation and the world. Presently 80% of the waste stream of the United States is disposed of in land fills, approximately 10% is recycled and 10% incinerated. The threat to ground water posed by landfill disposal makes this approach less and less desirable. The health problems associated with discharge from incinerators is also making this approach less desirable. Therefore other disposal methods must be given serious consideration. One potential disposal method which is being considered by Congress is storage of industrial waste on the deep ocean seafloor.

The Congress has tasked the Department of Defense (DoD) to "study the advantages, disadvantages, and economic and environmental viability of storing industrial waste in the abyssal plains of the ocean floor."

This project and associated tasks described in this proposal is a new start.

### **Project Description:**

The Department of Energy (DOE) funded an extensive effort termed Subseabed Disposal Program to assess the feasibility of sequestering high level nuclear waste in the deep ocean. In addition, there have been other studies conducted by federal agencies, industry, academia and private foundations addressing the issue of waste disposal on the seafloor. The Naval Research Laboratory (NRL) will conduct a literature search. The results of this search, where applicable, will be factored into this project.

The technical objective of this project is to: (1) identify environmental characteristics of abyssal plains which affect suitability for waste disposal; (2) select abyssal plain areas possessing these characteristics; (3) assess candidate waste handling technologies as to

engineering feasibility and reliability; (4) develop a survey plan to obtain a baseline of physical, chemical, biological and geological characteristics of a suitable area; (5) prepare a monitoring program; and (6) conduct an economic analysis of the deep ocean storage concepts.

This project will assess and document the advantages, disadvantages, and economic and environmental viability of storing industrial waste in abyssal plains. The technical approach will be to: (1) review past studies and concepts to store industrial waste on the seafloor; (2) compile and analyze existing oceanographic, biological, chemical, geological, geophysical and geotechnical data; (3) conduct numerical analyses and simulations to support the scientific, engineering and economic analysis and assessments; (4) identify risk areas from engineering, environmental and economic perspective; and (5) assimilate above information into a final report.

The approach will be implemented in five interrelated tasks. (These tasks are described in detail later in this text.) Task interdependencies will be identified early in the project execution to help focus effort. Intermediate results from tasks will be fed into other tasks during the execution of this effort to ensure completely integrated conclusions and recommendations.

The proposed work conforms to and enhances the environmental policy and objectives of the DoD, DOE and the national government in general. This effort will provide pertinent information required by Congress to address the critical national problem of industrial waste disposal.

There does not appear to be any ongoing studies of abyssal plain storage of industrial waste.

This project consists of five tasks: (1) Area Assessment, (2) Engineering Analysis and Assessment, (3) Site Survey Plan, (4) Monitoring Program, and (5) Economic Analysis.

Task 1. Area Assessment: Identification of areas suitable for waste storage will involve a number of factors. These factors include: (a) ocean environmental conditions which would result in waste containment in the storage area with minimal spatial dispersion; (b) areas where water depths exceed approximately 3000 m (10,000 ft); (c) areas with flat seafloor; (d) area with low biological activity; (e) areas within 1800 km (1000 nm) of the east, west and gulf coasts of the United States; (f) the effects of the oceanographic and meteorological conditions on ship design, transport and emplacement methodology; (g) post-emplacement capping methods and issues of seafloor stability; and (h) impact of various types of industrial waste on the local ecosystem. These factors will be addressed through compilation and analysis of available chemical, biological and physical oceanographic, geological, geophysical and geotechnical data from previous studies and assessments of waste disposal in the ocean by other government agencies, industry and academic institutions.

(a) Physical Oceanography Characteristics: Physical oceanographic and meteorological conditions will impact concepts for abyssal plain waste storage. Ocean currents are strong influences on the advection and dispersion of waste deposited on the seafloor. However, most oceanographic measurements are not obtained closer than about 100 m above the abyssal plain, so appropriate current information is scarce. Consequently, studies and proposals for deep ocean activities based on an assumption of quiescence requires further



analysis. Severe weather (hurricanes, typhoons and winter storms) will impact operational plans and logistics (scheduling, transportation, deployment concepts) and deep ocean dispersion of the waste materials.

To accomplish this task, this study will: (1) survey relevant studies, models, and databases for zones within 1800 km (1000 nm) of U.S. ports; (2) identify areas characterized by low flow conditions and geological stability; (3) provide a physical oceanographic description for the identified areas; (4) integrate this information with the biological, chemical and geological information; and (5) provide relevant data to site survey plan, monitoring program, engineering analysis and economic analysis.

(b) Chemical/Biological Characteristics: The study will assess the biological and chemical characteristics of abyssal plain areas which are geologically stable and hydrodynamically quiescent. Existing data bases will be assessed and interpretations made from studies of areas with similar depositional environments. This assessment will describe the existing status of benthic boundary processes which may be changed as a result of waste disposal. Some of these processes may be similar among areas, but others may be different, depending on the depositional environment, source materials and resulting biological communities on the seafloor. The site-specific, process-oriented approach will focus on biogeochemical fluxes across the sediment-water interface and diagenetic changes with depth in the sediment. Biological communities will be defined from a functional perspective in terms of their effects on fluxes of particles and dissolved chemical constituents, as well as the trophic-dynamic interactions among resident and transient organisms from size ranges of bacteria to megabenthos. It is known that "falls" of organic matter to the deep-sea floor attract benthopelagic animals which feed upon and transport wastes to adjacent areas. Therefore, it is important to assess the potential for vertical and horizontal transport of waste contaminants by animal migrations.

The waste characteristics and type of waste storage operations will be assessed with respect to the process-oriented approach as described for each defined area. Predictions will be made of how the existing conditions would be changed as a result of the interaction of industrial waste with the benthic ecosystem in terms of (1) nearfield fate and short-term effects, (2) farfield effects and (3) long-term effects.

(c) Geological/Geotechnical Characteristics: This effort will identify and describe areas of the abyssal plains that are geologically stable. The bathymetry, morphology, and geology of the seafloor will be examined and described with emphasis on those geological, geophysical, and geotechnical aspects that affect the suitability of the areas for waste storage.

The analysis will include a wide-ranging assessment of potential waste dispersal mechanisms: e.g., erosion by bottom currents, resuspension by biological activity, slumping due to oversteepening or earthquake loading and turbidity flows. Transfer of toxic materials from the solid to aqueous phases will be assessed: e.g., transfer from waste matrix in pore water flow driven by consolidation of deposits, and transfer by ion exchange in clay mineral double layers.

Task 2. Engineering Analysis and Assessment: The storage of industrial waste in abyssal ocean depths in a proposition dating back to the 1960's. The technology available for placing waste on the sea floor has matured from these early years. The Deep Sea Drilling Project demonstrated deep water dynamic ship positioning and the precise placement of drill stem

for borehole re-entry. The oil industry has transported progressively larger structures to deep water and successfully operated them. NRL recently deployed a large cable structure which spanned the total water column in an ocean depth of 5200 m. The DOE funded an extensive effort, the Subseabed Disposal Program, to assess the sequestering of high level nuclear waste in the deep ocean. These and other technologies can provide the bases for methods to store industrial waste in abyssal plains.

This part of the study will focus on technologies where waste dumping and dispersion in the water column is circumvented.

The assessment will consider dockside staging requirements, ship requirements, waste packaging, marine operations for transportation and disposal, and the hardware to place the waste on the sea floor. Reliability will be examined to evaluate risk associated with the operations. Numerical analyses will be performed where necessary to assure the proposed engineering concepts and approaches are technically sound and reliable. Environmental parameters from Task 1 will be incorporated into the assessment. Risk areas which impact the concepts from dockside staging through waste placement on the sea floor will be identified.

Necessary steps for the engineering assessment are: (1) perform literature search, (2) identify viable approaches, (3) conduct engineering evaluations, (4) perform risk analysis, and (5) identify implementation costs.

Task 3. Site Survey Plan: This task will provide the basis for planning and evaluating site surveys. Surveys are required to obtain a complete and up-to-date baseline of physical, chemical and biological characteristics so that change can be monitored in the storage site and surrounding area. The description of the selected area must include resident and transient fauna, bacteria, and geochemical, geotechnical and physical oceanographic conditions. The survey must be completed with sufficient lead time to evaluate site data and have monitoring systems in place. Methods and procedures for accurate description of the selected sites in terms of chemistry, biology, geology and oceanography will be analyzed and evaluated.

Task 4. Monitoring Program: This task will recommend a long-term monitoring program that will identify: (1) types of measurements; (2) frequency, location and methods of sampling; (3) data information system; (4) criteria for evaluating environmental change; and (5) the estimated cost of monitoring program. In structuring this program, the following factors will be considered; (1) waste material, (2) mode of dispersion in the sediments and water column, and (3) biochemical and geochemical reactions.

Task 5. Economic Analysis: Conduct an economic analysis to assess the viability of storing industrial waste on abyssal plains. The study will (1) review applicable past studies, (2) provide qualitative evaluation of future cost growth factors, (3) prepare assessment of cost of proposed concept, (4) prepare scenarios for economic assessment, (5) evaluate alternatives in scenarios, and (5) provide assessment of economic viability that summarizes information provided in previous tasks.

	(\$K)
Task 1	600
Task 2	600

Task 3	50
Task 4	100
Task 5	150

#### **Expected Payoff:**

The expected payoff of this project will be environmental, engineering, and economic information that the DoD and Congress can use in making decisions on the viability of storing industrial wastes on the deep ocean floor. In addition, NRL will recommend a site survey plan and monitoring program to be implemented if and when a demonstration program is initiated. This study does not address legal or sociological issues.

#### **Milestones:**

This project will take one year from date of receipt of funding to complete. The milestones below reflect this timeframe. NRL is prepared to provide a more detailed milestones chart for each Task.

Activity	Month from Start
Task 1	start at month 1; presentation/review at month 5; completion at month 9
Task 2	start at month 1; presentation/review at month 5; completion at month 9
Task 3	start at month 5; completion at month 11
Task 4	start at month 5; completion at month 11
Task 5	start at month 4; completion at month 11
Final Report	start at month 9; final report complete at month 12

#### **Transition Plan:**

The information from this project will be given to the DoD for transmission to Congress.

#### **Funding: (\$K)**

FY93  
1500

#### **Performers:**

Naval Research Laboratory  
Other government activities  
Industry, Academic Institutions

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## Conservation

Project Title	Page Number	Funding FY93 (K)
Natural and Cultural Resource Management		
Phased Array Ultrasonic Detection of Artifacts (A)	138	160
ITAM/Wetlands Integration (A)	140	450
Development of Overall Management Strategies for the Reduction of Noxious Plant Infestations with an Emphasis on Biological Control (A)	143	250
Land Scheduling and Management		
The Effects of Aircraft Overflights on Birds of Prey (AF)	146	80
Stabilization of High Use Training Areas in Cold Regions (A)	149	300
Digital Terrain Modeling and Distributed Soil Erosion Simulation/Measurement for Minimizing Environmental Impacts of Military Training (A)	151	800
Information Support for Environmental Management (A) *	154	750
Ecosystems Management		
Expanded Application of DNA Fingerprint Techniques developed as Genetic Diversity Measures of Aquatic Populations (EPA)	157	200
Assessment and Management of Risks to Biodiversity and Habitat (EPA)	161	1,000
The Role of Microphytic Soil Crusts in Desert Ecosystem Stability and Biodiversity (A)	164	250
Development of Regional Guidelines for Evaluating and Managing T&E Species Habitats on DoD Lands (A)	167	300
Methods for Propagation, Translocation, and Reestablishment of Threatened and Endangered Species (A)	169	350
LCTA/BCD Biological Diversity Sensitivity Analysis (A)	171	350
Fishing Enforcement/Stock Assessment and Marine Mammal Monitoring (N)	174	2,000
Marine Mammal Health (N)	178	249

Project Title	Page Number	Funding FY93 (K)
Identification, Assessment, and Mitigation of Impacts of Military-Related Chemicals and Pollutants on Threatened and Endangered Species (A)	186	525
Application of Biomarkers for Monitoring and Assessment of Sensitive Fauna in Ecosystems Impacted by Munitions Waste and Defense Related Material Application Sites (EPA)	190	900
Total		8,914

\* Congressional Interest Program

**SERDP Thrust Area: Conservation**

**Title:** Phased Array Ultrasonic Detection of Artifacts

**Problem Statement:**

The goal of this work is to develop an ultrasonic probe using phased array technology for the sub-surface detection and imaging of artifacts.

Currently, the reliability associated with the detection and location of artifacts is minimal. Often valuable finds are missed only to, at times, be found during construction causing delays and increased costs. Ultrasonic sound waves exhibit the non-destructive capability of being transmitted into the ground and probe beneath the surface by being reflected off of mediums of higher relative density (i.e. bone, ceramic, stone, glass).

**Project Description:**

Ultrasound techniques are in routine use for medical, engineering and oil exploration applications. Three dimensional or two dimensional (tomographic) imaging of everything from human brains to oil fields is now common place. The objective of this work is to develop a phased array of ultrasonic transducers which can accurately image sub-surface features of differing densities. For example, by analyzing the signal strength returned within specific time windows precise regions can be examined. By varying these windows the whole volume can be examined while excluding most interference reflections. Through computer imaging and enhancement the location of possible artifacts can be identified while also gaining information about their shape and dimension. An important application for the proposed technology is its potential use on an existing site for locating high density, historic, degraded, metallic and ceramic artifacts.

**Expected Payoff:**

To non-destructively probe beneath the surface to locate possible buried artifacts before construction begins. The potential also exists to more rapidly examine known archeological sites in order to better use limited excavation resources. Another possible use would be the location of underground utilities.

**Milestones:**

Activity	Completion Date
Survey commercial systems and services	FY93
Build test bed for transducer and imaging software testing	FY93
Build transducer/detector array	FY94
Wire computer interface	FY94
Develop control and imaging software	FY95

**Transition Plan:**

Once the capability of sub-surface detection has been shown field tests at known archeological sites should follow. The predictive capability should be compared to actual archeological findings under varying circumstances in order to determine reliability.

**Funding: (\$K)**

FY93	FY94
160	240

**Performers:**

Organization: US Army Construction Engineering Research Laboratories

Partners and Related Activities: Professors in both Electrical Engineering and Physics at the University of Illinois are engaged in research concerning ultrasonic sound waves. The work will be coordinated with the Tri-Services Cultural Resources Research Center.

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**SERDP Thrust Area:** Conservation

**Title:** ITAM/Wetlands Integration

**Problem Statement:**

The two goals to be accomplished are to identify information/data requirements necessary to support the Training Area Manager in accomplishment of his training mission while achieving full compliance with wetlands protection requirements in law as well as good general stewardship of wetlands resources and to integrate wetlands considerations into the Army-wide Integrated Training Area Management (ITAM) program.

In order to meet training mission requirements, Army Training Area Managers must maximize use of all available training lands. At the same time, they must comply with Wetlands regulatory requirements set forth in the Clean Water Act, and with the mandates of Executive Orders (11988) Floodplain Management and 11990 (Protection of Wetlands). In addition, many of the endangered species protected under the Endangered Species Act are associated with wetlands. Because of these potentially conflicting land use demands, Training Area Managers need:

- (1) Guidelines (standards) for inventorying, evaluating (functional analysis) and monitoring of wetlands on Army Lands.
- (2) Guidelines for evaluation of the impact of military operations on wetlands.

These guidelines can be effected through a wetlands data module incorporated into the ITAM program.

This project is new in the SERDP program, but complements on-going work by CECER under the ITAM program.

**STRAP Requirements Served:**

- (4.II.1.d) Guidelines for wetlands protection, restoration and management
- (4.II.1.c) Computer based wetland mapping system
- (4.I.1.a) Methods for standard, comprehensive, cost effective inventory and monitoring to fully characterize wetlands ecosystems

**STRAP Wetland/Riparian Ecosystem Work Units Served:**

- Effects of DoD Missions on Wetlands Ecosystem Components
- Integration of Site Specific Missions with Wetland/Riparian Ecosystems

**Project Description:**

This project will facilitate partnering of CEWES wetlands experts, CECER ITAM experts, and CECRL cold regions experts in order to integrate wetlands considerations systematically within ITAM. CECER, the lead activity for ITAM, has done some literature review relative to wetlands data needs for an ITAM wetlands module. CEWES has a long history of research and technical assistance in wetlands delineation, evaluation, management and restoration.



CECRL has done considerable work with cold regions soils, hydrology and vegetation, all of which could be important in developing a wetland module or ITAM.

The technical objective is to identify specific user (installation) requirements relative to wetlands protection and management, and then apply the wetlands expertise of CEWES, the ITAM expertise of CECER, and the cold regions expertise of CECRL in development of guidelines and procedures for meeting those installation needs.

There will be a five step technical approach:

Step 1. Evaluate Army user requirements for wetlands inventory, short and long term monitoring, and military impact management. This will entail visits to selected installations, and a user group workshop hosted by CEWES/CECER/CECRL.

Step 2. Identify/develop technical standards for wetlands inventory, monitoring and management. A review of existing information and techniques will be conducted. This will involve an extensive literature review and a CEWES, CECER, CECRL information exchange.

Step 3. Identify impacts of military operations on wetlands. Explore/develop techniques to experimentally and quantitatively evaluate and monitor impacts of military operations on wetlands.

Step 4. ITAM/Wetlands integration. CEWES/CECER/CECRL will cooperate in adapting wetlands requirements and guidelines to the ITAM program. This will include establishing a wetlands data base within the ITAM system, interfacing the ITAM database with appropriate wetlands databases available through CEWES, USFWS and others.

Step 5. Technology transfer. CEWES/CECER/CECRL will host user workshops to explain and implement the ITAM wetland module.

This report addresses wetlands concerns set forth in the Tri-Service Environmental Quality Strategic Plan Program, i.e., "Effects of DoD Missions on Wetlands Ecosystem Components" and "Integration of Site Specific Missions with Wetland/Riparian Ecosystems."

#### **Expected Payoff:**

This project will provide tools needed by both Training Area Managers and Natural Resources Managers at installations to better perform their missions. In addition, it provides an opportunity for CEWES, CECER and CECRL to lay the groundwork for improved cooperation and efficiency in meeting the needs of our military customers served by the ITAM, cold regions, and wetlands programs.

#### **Milestones:**

Document Army user requirements for wetlands inventory, short and long term monitoring, and military impact management.	FY93
Guidelines on technical standards for wetlands inventory, monitoring and management.	FY93
Identify impacts of military operations on wetlands.	FY94

ITAM/Wetlands integration.  
Technology transfer, including workshops.

FY95  
FY95

**Funding: (\$K)**

FY93	FY94
450	500

**Performers:**

Performers will include personnel of CEWES, CECER, CECRL, the U.S. Fish and Wildlife Service, and Army installations.

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## **SERDP Thrust Area: Conservation**

**Title:** Development of Overall Management Strategies for the Reduction of Noxious Plant Infestations With an Emphasis on Biological Control

### **Problem Statement:**

Many noxious terrestrial and aquatic plants cause serious problems for military bases and training installations across the country. Problem plants include the terrestrial species snakeweed, knapweed, leafy spurge, various thistles, seepwillow, silver leaf nightshade, tansy ragwort, etc., and the aquatic plants, waterhyacinth, waterlettuce, hydrilla, Eurasian watermilfoil, water chestnut, etc, among others. Problems mainly arise because of the growth characteristics of these plants which enable them to reach very large population levels relatively rapidly thereby displacing and subsequently eliminating native vegetation. This in turn causes significant impacts to native wildlife including the elimination of endangered species, disruption of delicate ecosystems by the replacement of native vegetation, decreases in land use and value on the installations as well as adjacent communities, reduction of recreational uses, hinderance of navigation along waterways, increased water loss, as well as increases in human health hazards associated with expanding mosquito breeding habitats. In addition, the movements of large amounts of equipment and men associated with military training exercises only worsens the problems caused by noxious plants because of the potential for plant dissemination by such movements. Traditional control procedures mainly involve the use of chemical applications but these offer at best only short term solutions and their use is becoming increasingly more environmentally sensitive.

There are now more environmentally acceptable techniques and integrated procedures for noxious plant control. These mainly involve the use of biological control agents and offer environmentally acceptable and in many cases long term answers for weed management. The use of biological control gained public acceptance as early as 1902 with the release of flower and fruit feeding insects for the control of *Lantana camara*. These insects successfully controlled the invasion of lantana in many areas of Hawaii. Since that time over 190 insects have been released to manage 86 weed species with over half of these attempts considered successful. The use of biocontrol for weed management has not only been confined to the terrestrial environment. Many successes have been achieved in the aquatic habitat. These have included the release of 12 insect species to control 4 problem aquatic plants since the beginning of the aquatic plant biocontrol program in 1959. Currently biological control is rapidly becoming recognized as an important and viable alternative management strategy for weed control. Since 1987 alone over 40 insect species have been introduced in the U.S. for the control of >15 weed species.

### **Project Description:**

The proposed work will concentrate on developing overall management strategies for controlling noxious vegetation mainly through the use of biological control techniques. While emphasis will be on the use of biological agents the proposed work will also develop computer-based systems that allow minimally trained military personnel to make informed management decisions concerning the control of noxious vegetation on a site by site basis using all of the available management options. Three major areas will be stressed initially; 1)

identification of major noxious plants and their associated problems on major military installations across the country, 2) development of overall guidance strategies based on currently available technologies, and 3) development of computer based management tools that incorporate information gained in objectives 1 and 2 to aid operational personnel in choosing the appropriate biocontrol agent or as the situation warrants, more traditional control tactics (i.e., mechanical, chemical, etc.) on a site by site basis. Further long term biocontrol demonstrations will be accomplished via transition research.

The work will progress along several lines. The first will be to identify problem vegetation on various major military installations and categorized on a regional basis. A database of the noxious plants will be developed and currently used control procedures compiled based on information supplied by military personnel as well as federal and state agencies. The problem plants will then be matched to biocontrol agents that are currently being used operationally across the country. This information will then be used to develop a computer-based system that will allow minimally trained personnel to make informed decisions concerning plant identification, determinations of economically important plant infestations, recommended control procedures, and operational biocontrol agents available. The system will be a PC-based expert system using high resolution color graphics for plant and biocontrol agent identification and regional databases for control recommendations.

The second line of work will be to begin demonstrating the potential of using biocontrol agents for noxious weed management. Based on information gathered on noxious plants and availability of operational biocontrol agents sites will be selected across the country for field demonstrations of certain plant/biocontrol agent management strategies. Sites selected will depend on noxious plant infestation levels, severity of the problem, expected control time for the agents selected, and availability of the agents. Demonstrations will be used for determining the suitability of using specific agents or complex of agents for management.

Developing an overall management plan for noxious plant management that emphasizes the use of biologicals will certainly lower the use of chemical applications for control.

Developing a guidance plan that incorporates all existing control technologies will foster an integrated approach toward the management of noxious vegetation and will afford the best control possible with minimal use of chemical applications.

#### **Expected Payoff:**

The use of an integrated approach using computer-based systems that stress the use of biologicals for noxious plant management is the best strategy for plant control. Such a management plan will allow minimally trained personnel across the country to make similar informed control decisions on a site by site basis concerning appropriate and environmentally correct procedures for plant management. This plan will allow the integration of all existing control technologies which will allow for reduced chemical applications, best possible combination of control techniques with longer control time frames.

#### **Milestones:**

Develop list/database of noxious plant problems  
Summarize existing control technologies

FY93  
FY93

Develop list of operational biocontrol agents	FY93
Develop first generation computer system	FY93
Begin small scale biocontrol field demonstrations	FY93
Second generation computer system (all components)	FY94
Evaluation of field demonstrations	FY94

#### **Transition Plan:**

The use of biologicals is a long term commitment especially considering that most agents do not achieve control for at least 5 years. For full implementation of an overall management plan that stress the use of biologicals more than 2 years is needed for effective evaluations and subsequent recommendations. Future plans will mainly involve testing various combinations of biological control agents with the goal of identifying which agents are appropriate under what environmental conditions. New information will then be incorporated into a revised computer-based decision system. This study will provide information relevant to four currently unfunded work units in Thrust 4.I. range/training area revegetation: 1) weed control technology, 2) weed control demonstrations, 3) weed control guidance, and 4) management guidelines for forest pest control.

#### **Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>	<b>TOTAL</b>
250	250	500

#### **Performers:**

U.S. Army Corps of Engineers, Waterways Experiment Station; Environmental Laboratory  
 U.S. Department of Agriculture, Agricultural Research Service  
 U.S. Fish and Wildlife Department

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**SERDP Thrust Area: Conservation**

**Title:** The Effects of Aircraft Overflights on Birds of Prey

**Problem Statement:**

The goal of this project is to verify predictions of a previous 6.3A effort regarding the effects of aircraft noise on birds of prey or raptors (hawks, eagles, falcons, etc.) and to fill in the technological gaps in the interim model.

The Air Force is required to assess the impact of proposed aircraft operations on the environment. Many of the assessments accomplished to date contain unsubstantiated remarks concerning the adverse effects of aircraft noise on wildlife. Prior to 1989 noise studies on wildlife were not well controlled or planned. In 1989 the Air Force began performing several 3-4 year studies on the effects of aircraft noise on wildlife species. The results from these studies are proving very useful for environmental planners at the major command and Air Staff level to defend the Air Force's requirements to maintain low altitude Military Training Routes (MTR).

Due to issues raised during public scoping meetings and documented concerns with the US Fish and Wildlife Service (USFWS) and the National Park Service (NPS) there is concern that aircraft overflights may disturb nesting raptors. The Air Force embarked on a project in 1989 to review the current literature regarding the effects and, if feasible, develop an interim model to predict the effects. The interim model was documented in 1990. Since the model is purely hypothetical, it must be validated with empirical data.

**Project Description:**

The technical objective of this project is to develop a validated dose-response model on the effects of aircraft overflights on birds of prey. The technical approach to accomplish the objective will be to perform field studies on species of interest in an attempt to validate the current model.

Several tasks will accomplish this objective. In Task 1, a study protocol will be developed in cooperation with the USFWS to perform valid field studies to detect differences of 5-30% productivity rates in spite of large variances in nest success. The study design will take into account such factors as habituation rates, prey abundance, and changes in parental behavior that could affect productivity. This first task will examine possible study locations and make a recommendation for the best sites near an Air Force installation to perform such a study.

Task 2 will be designed to make observations of aircraft overflights in the vicinity of nesting raptors. This task should be performed over a two year period at a minimum to determine the effects of noise and visual intrusion on productivity.

Task 3 would attempt to address the effects of aircraft overflight noise on threatened or endangered raptor species, such as Peregrine Falcons and Bald Eagles. This task would form a subset of data obtained from Task 2 where nonthreatened and nonendangered species would be studied.

Task 4 will involve making changes to the current dose- response model and inserting the improved model into the latest version of the Assessment System for Aircraft Noise (ASAN). ASAN is a software tool to assist environmental planners in preparing Environmental Impact Assessment Process (EIAP) documents.

#### **Expected Payoff:**

The Air Force will benefit by having a validated model to assess the impact of aircraft noise on raptors. This will greatly assist environmental planners in developing timely EIAP documents and providing answers to questions raised by the general public, USFWS and NPS. Currently, the USFWS can and has stopped proposed actions with formal Section 7 consultations in accordance with the Endangered Species Act. The goal of this project would be to reduce the concerns raised during these formal consultations and speed up the EIAP.

#### **Milestones:**

Task 1: Research protocol and recommended study sites	FY93
Task 2: Experimental data on nonthreatened and nonendangered species	FY95
Task 3: Experimental data on threatened and endangered species	FY96
Task 4: Dose-response model validated and improved model inserted into ASAN	FY96

#### **Transition Plan:**

The dose-response model resulting from this effort would replace the current interim model in ASAN. ASAN is scheduled to begin transition in FY93. Since ASAN is designed in modular form, there will be minimal risk.

It will be necessary to coordinate aircraft overflights with the nearest operating command to the study site. Since several previous studies similar to this proposal have been accomplished, these procedures are well known.

#### **Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
Task 1	80	
Task 2		200

**Performers:**

Air Force - AL/OEBN

US Fish and Wildlife Service (with interagency agreement)

Research contractors (e.g. BBN Systems & Technologies, Wyle Labs, Biosystems Inc.)

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## **SERDP Thrust Area: Conservation**

**Title:** Stabilization of high use training areas in cold regions.

### **Problem Statement:**

Military training installations represent some of the most intensively used lands in the United States. Military vehicular traffic has a very destructive direct impact on the vegetation. Destruction of the vegetation may, in turn, lead to soil erosion, sedimentation of streams and lakes, loss of training realism and reductions in the carrying capacity of the land. To date, research has not addressed the potential to develop plant varieties that are more resistant and resilient to military training impacts.

For plants to be successful colonizers on these lands, they must be able to tolerate both poor environmental conditions (cold, infertility, and drought) and the soil compaction and wear associated with training excursions. Plant characteristics which would be beneficial for growth and survival in these areas include a rapid germination and establishment rate, tolerance to poor soil conditions, ability to spread into denuded areas where intensive training occurs and be cost-effectively able to establish.

### **Project Description:**

Army training sites have been in existence for 50 years or more. Plants with the desired characteristics are probably surviving at the present time on these sites. Up until this time, no information has been collected on what characteristics are important for plant survival on these sites. This is a labor intensive effort and will include site visits and seed collection of promising species. The collected seeds will be germinated in the greenhouse and interpollinated with other promising clones to develop improved cultivars of the species being studied. Once improved clones are developed, they will be placed where their parents originated, to determine improved performance.

Plant selection techniques will follow those used in the turfgrass industry for breeding improved lawn grasses. This includes locating clones of plants that have performed well at existing training lands. A small plant selection program using a similar procedure has already been started at CRREL and has shown that an improvement in the establishment characteristics of switchgrass, a native American species, was observed in only one year. Therefore, there is a great potential to develop beneficial characteristics in grasses and legumes in a short amount of time.

### **Expected Payoffs:**

The Army manages many acres of training lands and reduced soil erosion of these sites is the primary goal of our stewardship. New cultivars developed through this program will be reproduced in concert with seed houses and used to restore degraded training areas, thus reducing soil erosion. Newly developed cultivars will also be available for improvement to fit other areas important to the Army's mission such as gunnery ranges, drainage channels, etc. These new cultivars will also have a place in other areas with similar problem soil types, such as gravel pits, roadsides, and dredged areas along waterways.

**Milestones:**

Review literature and collect promising plant clones	FY93
Continue collection and begin interpollination	FY94
Select promising clones and begin field studies	FY95

**Funding: (\$K)**

FY93	FY94
300	300

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## **SERDP Thrust Area: Conservation**

**Title:** Digital Terrain Modeling and Distributed Soil Erosion Simulation/Measurement for Minimizing Environmental Impacts of Military Training

### **Problem Statement:**

The objective of this project is to develop improved analytical tools to assist military land managers in predicting the amount and spatio-temporal distribution of soil erosion and sediment deposition within watersheds, and suspended sediment as a non-point source pollutant in waterways.

Soil erosion and consequent siltation of streams and reservoirs has long been recognized as a major environmental concern on military installations. The problem is exacerbated where intense training and testing activities cause severe recurrent disturbance to the soil surface and where waterborne sediments act as carriers to toxic pollutants. Minimization of soil erosion and its consequences requires reliable prediction of the spatial and temporal distribution of the erosion and sediment routing processes. Most existing approaches to soil erosion and sediment transport rely on lumped-parameter semi-empirical relationships developed for agricultural fields. Such approaches are unable to provide consistent and accurate results for watershed-scale erosion and runoff processes. Another primary limiting factor is the inability to accurately represent the terrain in a digital format consistent with high resolution watershed-scale erosion and sediment transport modeling. Available digital elevation models do not fulfill the requirements for adequate resolution, accuracy and hydrologic soundness necessary for terrain analysis in general and erosion modeling in particular. In addition, there are no existing procedures to account for the frequency and distributional patterns of disturbances that occur on military training and testing facilities. The development of new-generation technical tools to model distributed surface erosion and runoff in complex terrains typical of military training and testing lands is a necessity. Such tools will provide a basis for predicting the environmental impacts of military-related activities and for the optimization of land rehabilitation programs for installations. Compliance with the Clean Water Act will be ensured and realism of the training and testing environment will be preserved.

### **Project Description:**

This effort supports the Conservation Pillar of the Tri-Service Strategic Environmental Research and Development Plan. Specifically, this program will provide total and partial fulfillment of the program lines "Digital Elevation Data for Modeling Watershed-Scale Erosion Processes" and "Adapting New Generation Water Erosion Models to Military Land," respectively.

Recent studies have shown that lumped-parameter modeling approaches are often erroneous, particularly for larger areas typical of many military facilities. Recent advances in computer modeling, as well as spatial data bases make spatially-distributed physically-based erosion and deposition modeling the logical trend of the future. In such transition, the following parallel thrusts to the problem are proposed:

- 1) Enhancement of existing tools by improving methods of topographic analysis and then application of unit stream power theory to determine critical areas with highest erosion rates, deposition rates, and suspended sediment concentrations.
- 2) Simulation of rainfall-runoff processes through the application of numerical techniques with the addition of sediment and contaminant transport routines. This approach represents the new generation of water erosion models and more accurately predicts the spatial and temporal distribution of erosion events. Furthermore, by predicting the outflowing runoff and sediment, the off-site impacts such as flooding and siltation can be predicted. Incorporation of remotely sensed data, such as rainfall intensity and soil moisture content, can provide the opportunity to simulate rainfall-runoff-sediment processes in a real time environment.
- 3) Field measurements of soil/hydrologic parameters and in-stream sediment concentrations for validation of the proposed algorithms.

#### **Expected Payoff:**

Potential benefits that may be derived from this project include 1) improved capability to generate digital elevation models and to perform topographic analyses for various terrain related applications; 2) improved capability to estimate erosion/deposition rates as an input for choosing the optimal land use management and rehabilitation programs; 3) spatially dynamic modeling of erosion and deposition to assist land managers and trainers in optimizing training schedules, delineating training areas, and monitoring changes over time; and 4) acquisition of appropriate tools to simulate erosion control structures for improving their effectiveness.

#### **Milestones:**

Develop enhanced interpolation methods for computation of high resolution (5-10m), hydrologically sound digital elevation models implemented in the Geographic Resources Analysis Support System (GRASS).	FY93
Install sediment data collection platforms and initiate in-field soil and cover parameter data collection.	FY93
Develop algorithms and models for estimation of erosion and deposition potential in complex watersheds. Integrate the models in GRASS.	FY94
Develop enhanced systems that will allow land managers to design sediment control structures.	FY94
Further enhancement and calibration of dynamic models using field and laboratory data to provide a new generation of land management models for military use.	FY95

Deliver interactive computer programs functioning in the GRASS environment to predict soil loss and sediment yield based on projected land uses, soil characteristics and climatic parameters. Also, computer models that will generate erosion/sediment control structure alternatives, designs and placement.

FY96

**Transition Plan:**

The work will be conducted cooperatively by the U.S. Army Construction Engineering Research Laboratories and the Waterways Experiment Station. The work will be coordinated with the University of Illinois, U.S. Air Force Air Weather Service, Soil Conservation Service, Environmental Protection Agency, and Agricultural Research Service.

**Funding: (\$K)**

FY93	FY94
800	1000

**Performers:**

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## **SERDP Thrust Area: Conservation**

### **Title: Information Support for Environmental Management**

#### **Problem Statement:**

Conservation of plant and animal community habitats is a difficult task because of competing alternatives for land. A better understanding of the interdependence of natural biological systems and man-made physical and biochemical systems is the primary concern of sustainability. All DoD lands, ranging in activity from hosting a military installation to reserves for recreational land, encounter a daily requirement to efficiently manage natural resources. DoD Land managers must find a way to best optimize the support to the military while still protecting the natural resources for which they are the responsible stewards.

The environment has a finite carrying capacity as well as finite capacity to process waste to non-toxic levels. Monitoring the biological community against mankind's specific values, goals, and expectations provides a basis for evaluating sustainability of a geographic area. Environmental management techniques must be developed to efficiently control available socio-economic options in an effort to sustain or even enhance biological ecosystems. Effective selection of these options can best come from closely examining our past experiences with environmental decisions. An examination of past decisions made within a specific geographic environment and determining what and why it has happened is a methodology designed to help formulate solutions for sustainable development and to provide insight for the present and future stewardship of our natural resources.

#### **Project Description:**

The proposed project involves the development of an environmental manager's decision support system for the management of habitats on DoD and other government owned lands. To understand the cumulative impact of natural processes and various DoD missions, basic ecological principals and data demonstrating change over a long time-frame will be analyzed.

Valuable historical habitat data over an 80 year period is available for the Jornada Experimental Range, a USDA/ARS site adjacent to the ecologically sensitive DoD installations of White Sands Missile Range (WSMR) and Ft. Bliss. Jornada data offers a variety of scaled information (i.e. plant crown plots for 104 one square meter quadrants and vegetation data across the entire range). A detailed time series evaluation of the Jornada's habitat data will assist in the development of well conceived, well grounded decision making tools. The proximity of the Jornada Experimental Range to the major installations of WSMR and Ft. Bliss represents an opportunity to establish a baseline decision support systems in a neighboring system of semi-arid land habitats that has been generally untouched by military activity.

Phase I of this project develops a methodology for prototyping a grounded analytical framework and decision tool set for semi-arid land habitat management. During Phase II, inferences will be drawn against neighboring Ft. Bliss and White Sands Missile Range habitats as they relate to the Jornada. Phase II will also include a) experimental validation of conclusions concerning habitat dynamics developed over the Jornada data with application to

Ft. Bliss and White Sands, b) the capture of existing ecological process models relevant to semi-arid habitat analysis, c) the exploration of decision parameters relevant to habitat management for both training and non-training areas of White Sands and Ft. Bliss, d) identification of non-restorable habitat changes resulting from DoD installation activity, and e) the initial assembly of an environmental manager's tool set within a fusion architecture such as FALCON.

Phase II level of effort is envisioned as integrating the semi-arid military habitat environmental tools developed during Phase I and II into a management plan to be implemented on TECs future Environmental Decision Support System. Vegetation stress identifiable from remote sensing signature responses (developed under complementary SERDP efforts) will be examined to search out possible habitat change caused from hazardous material disposal. Military installations, in addition to Ft. Bliss and White Sands, will be explored which have been recommended by the Army Environmental Center (AEC) as critical lands for characterization of environmental problems. Future site(s) will be determined during Phase II.

#### **Expected Payoff:**

A large and diverse customer base is expected, including any DoD land holder, the AEC, and the Bureau of Land Management of the Department of the Interior. Standardization of semi-arid environmental management decisions is a pursued goal. Reducing subjectivity in the decision making process should both maximize the natural resources and reduce the cost of their administration. For example, estimated administrative cost savings to be derived from remote sensing for an initial site characterization of DoD lands is 25% of time and labor costs. "What-if" decision forecasting by a resource manager is an anticipated payoff. Contributions in fulfillment of the DoD Integrated Training Quality Area management program and the Tri-Service Environmental Quality Research and Development Strategic Plan (the conservation pillar in particular) are foreseen. Designation of GO/NOGO areas for training exercises based on environmental risk to the habitat are planned. Findings derived from this project are to be generalized to other geographic areas with similar physiographic characteristics.

#### **Milestones:**

FY

##### **Phase I (1 year)**

Completed sample Jornada data set	94
Demo prototype TIES environmental data exploitation	94
Demo soft/hard copy habitats over map backgrounds	94
Demo climate correlation with habitat change maps	94
Complete detailed analysis of Jornada data	94
Ft. Bliss & White Sands data assessment report	94
Ft. Bliss & White Sands training area assessments	94
Provide seasonal change algorithm using FALCON link	94
Deliverables: final digital Jornada data, GIS maps habitat interpolation/extrapolation methods, climate data, WSMR/Ft. Bliss data, Jornada habitat products, analytic and fusion algorithms, fusion prototype, encapsulated models, final report on analysis methodologies employed	94

Phase II (estimated 2 year effort)	FY
Complete statistical correlation of data	95
Systems evaluation for optimal environmental management	95
Transfer decision parameters at Jornada to WSMR/Bliss	95
Complete examination of DoD training area considerations for habitats	95
Validation of Jornada conclusions to WSMR/Bliss	96
Complete development/integration of ecological process models	96
Phase III (estimated 2 year effort)	
Complete examination of additional installation habitat patterns	97-98
Incorporate vegetation stress into habitat definition	97
Integrate into Environmental Decision Support System	97-98

#### **Transition Plan:**

The Coalition for International Environmental Research and Assistance (CIERA) offers the Army an excellent vehicle in which to work in conjunction with university level research laboratories from across the nation and to pass on DoD expertise through the university into the public sector. Future transfer of technologies will be coordinated through organizations such as the DoD Tri-Service Environmental Working Group.

#### **Funding: (\$K)**

##### **FY93**

- 500 CIERA (DoD Appropriations Bill, 1993)
- 250 TEC, (The original proposal submitted by CIERA was re-scoped by TEC at the request of the Office of the Director of Defense Research and Engineering, Director, Environmental and Life Sciences. Total TEC Phase I participation will be \$350K, \$100K of which will be leveraged from complementary GIS endeavors, thereby reducing additional funding required to \$250K.)

#### **Performers:**

The broad based expertise of both CIERA and TEC will be actively applied to this project. Other Corps Labs will be invited to contribute where appropriate in Phase II & III efforts. CIERA coordinates and provides university level research institutions at overhead rates much lower than those available under standard government-to-university contracts. Ft. Bliss and White Sands Missile Range resource managers will be actively consulted during the project as will personnel from the AEC. Overall project management will be jointly provided by CIERA and by TEC.

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## **SERDP Thrust Area: Conservation**

**Title:** Expanded Application of DNA Fingerprint Techniques developed as Genetic Diversity Measures of Aquatic Populations

### **Problem Statement:**

The aim of this proposal is to expand the application of DNA fingerprint techniques being developed in a Phase I SERDP project as genetic diversity measures for aquatic populations, primarily fish, to include additional terrestrial populations of both animals and plants which inhabit contaminated and/or ecologically sensitive areas impacted by military installation and activities.

The genetic diversity or gene repertoire of a population reflects its intrinsic robustness. Loss of genetic diversity leaves a species less able to adapt to new stressors and, therefore, loss of population genetic diversity can foreshadow species loss, with resultant loss of biological diversity within the community. Loss of diversity resulting from habitat destruction and pollution is a major concern in wildlife populations.

The technique of DNA fingerprinting is being widely used to determine the identity and relatedness of individuals (particularly humans), and is also attracting attention as a tool for assessment of genetic variations within and between populations. It is possible to demonstrate genetic differences between individuals at the DNA level, even in species that are otherwise genetically uncharacterized. The summation of DNA fingerprint differences of many individuals provides a measure of genetic diversity in the population from which those individuals are derived. Undisturbed natural populations tend to maintain a high degree of diversity or polymorphism, but any environmental stress that eliminates a large fraction of individuals from the breeding population can eliminate (by pure chance) important genetic variants. The reduced genetic repertoire in generations subsequent to this bottleneck leaves that population more vulnerable to future stresses. Therefore, quantitative measures of genetic diversity can be useful as indicators of past environmental insult as well as criteria for targeting potentially sensitive, i.e., genetically homogeneous, populations.

Although the genetic diversity measures developed for aquatic populations in the Phase I SERDP project are in principle applicable to any species, in practice, each new species examined will require optimization of laboratory protocols to produce valid fingerprint data as well as considerable labor involved in fingerprinting the large number of individuals representing a statistically valid sampling of several populations. Therefore, additional funding enhancement is requested to expand this work to include additional species and habitats.

### **Project Description:**

Two different, but complementary fingerprinting techniques for use in species of fish are currently being adapted. The first method relies on the presence throughout the genomes of most organisms of repeated short sequences, with the repeat numbers genetically determined, but extremely variable within the population. (These are called VNTRs - variable number of tandem repeats.) Bands visualized on a Southern blot of genomic DNA with radiolabeled

probes specific to the repeat sequence are characteristic of the individual. Comparison of the banding patterns among individuals from a population yields a measure of genetic variation within that population. Comparisons across populations yield measures of relative genetic variation and also of the degree genetic relatedness of the populations. This method is being applied to a test sample of DNAs purified from more than seventy individual brown bullhead catfish representing three populations from both polluted and clean areas.

The second fingerprinting method is a PCR (polymerase chain reaction) based technique. In this method, bands are produced by preferential amplification of segments of DNA that happen to be bracketed by sequences complementary to the synthetic DNA oligomers used as primers in the reaction. This is termed the DAF or DNA amplification fingerprint.

Using the raw fingerprint data from both of these methods, several mathematical treatments for assessing DNA fingerprint diversity are being examined and compared in order to determine the best statistically valid approach. This part of the effort is being done in conjunction with Dr. Vicki Hertzberg with a Cooperative Agreement funded by Phase I SERDP.

The technical objective is to extend DNA fingerprint analysis capability to additional species, particularly terrestrial animals and plants. It is anticipated that each additional species will present its own unique technical quirks to be overcome and that each population examined will present some unique parameters to be dealt with in the mathematical comparisons. In short, the goal is to make this method universally applicable.

This capability will be applied to a number of ecologically significant situations, including but not limited to: monitoring of populations in sensitive areas over time in order to demonstrate maintenance, loss or recovery of diversity over time; comparisons of populations in separate habitats, i.e., clean vs. dirty sites; analysis of the genetic makeup of populations recolonizing reclaimed areas to determine their degree of similarity to the original displaced populations and the surrounding endemic populations.

The technical approach will consist of continued application of both fingerprinting methods outlined briefly above and extension of these methods to new species. Full development of the newer DAF method is highly desirable because it requires only a minute sample of tissue, allowing non-invasive analysis of individuals. It also offers the potential capability of fingerprinting preserved archived tissue samples, allowing comparisons between contemporary and historical populations.

The methods will be validated by comparison of results obtained by both methods; measures on defined stocks of animals or plants in which the degree of inbreeding is well characterized; analysis of field populations of known exposure history and for which clinical markers of exposure have been determined; and, when possible, comparison with genetic diversities calculated from protein polymorphisms.

Development of statistical analysis protocols will proceed concurrently with laboratory methods development. The raw data will consist of digitized fingerprint profiles obtained by automated scanning with a video densitometer. Statistical approaches will deal with internal assay uncertainties and controls as well as the parameters of population sampling and

comparison.

Ever-increasing liaison with field ecologists who are experienced with and possess detailed knowledge of each relevant population is expected. When appropriate, these interactions will be formalized as cooperative agreements. This will provide detailed expertise and assistance in field sample collection.

**Expected Payoff:**

This method will provide a rapid, non-invasive, and cost effective monitoring method in the form of an assessment of population genetic robustness for virtually any species, animal or plant, aquatic or terrestrial. It is anticipated that it can be modified into a commercially available, field usable tool and marketed via a CRADA.

**Milestones:**

FY93: Validation of Methods: Comparison of fingerprint patterns from inbred and outbred populations of known pedigrees. Development of methods for statistical comparison. Test and apply methods with laboratory *Peromyscus* colony. Explore methods for plants.

FY94: Validation: Comparison of fingerprints of terrestrial plants and animals of known pedigree with those of random field collected individuals of the same species. Continued development and application of statistical methods.

FY95-96: Applications of developed methods to field situations.

**Transition Plan:**

Enhancement of Phase I SERDP project.

**Funding: (\$K)**

FY93	FY94
200	200

Previous funding: SERDP Phase I funds- \$300K

**Performers:**

U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory - Cincinnati, Ecological Monitoring Research Division - Annette C. Roth, Ph.D.

Technology Associates Inc.: Non Agency support scientist: David L. Lattier, Ph.D.

Department of Environmental Health, University of Cincinnati, by Cooperative Agreement: Vicki Hertzberg, Ph.D. (Statistical Methods)

Biomedical Research and Development Laboratory, Ft. Detrick Dept. of Army - Dr. Hank Gardner, Dr. E. Baumel by Interagency Agreement.

**Technical Point of Contact:**

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Environmental Monitoring Systems Laboratory - Cincinnati  
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## **SERDP Thrust Area: Conservation**

**Title:** Assessment and Management of Risks to Biodiversity and Habitat

### **Problem Statement:**

The goal of this project is to develop the technical information and data bases needed to assess and manage risks to biodiversity

Biodiversity, in the simplest terms, is the variety of life and its processes. Society recognizes a large variety of aesthetic, economic, conservation, and educational values associated with biodiversity. All of these are dependent on the following "first principles." Biodiversity is a manifestation of genetic diversity. It is the primary raw material that is filtered by natural selection, resulting in evolutionary and ecological adaptation of biota to environmental conditions. Minimizing additional loss of biodiversity will provide the best assurance that biota will adapt to the ever increasing rate and spatial extent of environmental change.

Traditionally, the management of biodiversity has focused on rescuing rare, threatened or endangered species from the brink of extinction. Huge sums have been spent on recovery programs for a small number of species. While there are strong conservation arguments for preserving these species, the effort expended has been out of proportion to the contribution that these species make to the genetic diversity, and therefore the fitness of the biota as whole to adapt to environmental stress.

### **Project Description:**

This research will develop and test a new risk based paradigm for identifying those areas having species assemblages which contribute the greatest genetic diversity to the biota of their biogeographic regions and then managing those areas to sustain biodiversity. The paradigm is implemented in two stages and at two greatly different spatial scales. First, priorities for management action are identified by comparative risk assessment across spatially extensive biogeographic regions. This permits cost effective targeting of more intensive diagnostic and remediation efforts, allows accurate evaluation of the many species that have extensive geographic distributions, and avoids the pitfall of instituting protection at the local level, only to have cumulative effects of actions in the surrounding landscape undermine these efforts.

Secondly, specific remedial action plans are developed and implemented at a finer spatial scale (i.e., ecological subregions within a state) than the comparative risk assessment. At this scale, landscape level management approaches are needed. Attention will be directed to ameliorating the adverse effects of habitat fragmentation, reducing other forms of anthropogenic stress, restoring habitat, and evaluating the land management tradeoffs required to sustain biodiversity.

The initial technical objective will be to quantify relative risks to biodiversity by biogeographic region and landscape type with emphasis on DoD's role. Then to propose management options for high priority areas.

This research will initially categorize and map the species diversity and environmental diversity of each of about 12,000 sampling units (hexagons) based on the Environmental Monitoring and Assessment Program (EMAP) sampling grid covering the conterminous United States. The process will include (1) compilation of The Nature Conservancy's detailed vertebrate species distribution and attribute data for each hexagon, (2) compilation by hexagon of attributes of environmental diversity from remotely sensed land characterization data [AVHRR, TM or MSS based, depending upon results of pilot studies], and (3) analysis of the species and land characterization data by different ecological weighing methods, spatial analyses, multivariate statistical pattern analyses, and protection optimization methods. This information, along with stressor data compiled from existing databases [TIGER; USGS LUDA; USDA NASS, ERS, NRI, FIA; USDI BLM] will be evaluated and synthesized to quantify relative risks to biodiversity by region and landscape type. Overall patterns that lead to high importance and vulnerability of natural landscapes and biodiversity will be identified.

#### **Expected Payoff:**

Benefits include (1) establishment of baseline conditions concerning species distributions and their relationships with environmental diversity, (2) comparative risk assessment for biodiversity which identifies priorities for attention by the diversity of public and private land managers whose coordinated efforts will be necessary to sustain biodiversity and (3) testing of methods that hold promise for significantly reducing costs of habitat monitoring, evaluation, and management. Potential users will include virtually all land stewardship organizations concerned with the value of natural biotic resources.

#### **Milestones:**

Compilation of data bases	FY93
Data analysis	FY94
Synthesis and final report preparation	FY95

#### **Funding: (\$K)**

FY93	FY94
1,000	1,000

EPA funding to date has been about \$600K.

#### **Performers:**

In recognition that loss of biological diversity can only be effectively addressed through cooperation of vested interests, EPA has formed a biodiversity research consortium to develop the technical information and data bases needed to assess and manage risks to biodiversity. Initially, membership in the consortium includes the US Fish and Wildlife Service, USDA Forest Service, USDI Geological Survey, and The Nature Conservancy. Through this proposal, the Department of Defense will become a participant in this interagency consortium. Additional organizations will be added, much as the "Partners in

Flight" consortium has been created for neotropical migratory birds.

**Technical Point of Contact:**

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\* Note: The SERDP Scientific Advisory Board provided specific guidance to this project. Their position statement on this effort may be found in a separate section within this document; see "Table of Contents."

## **SERDP Thrust Area: Conservation**

**Title:** The Role of Microphytic Soil Crusts in Desert Ecosystem Stability and Biodiversity

### **Problem Statement:**

The objective of this project is to develop a basic understanding of the physiological processes of desert soil microphytes in the hope of identifying precise linkages between the decline or destruction of microphytic soil crusts and the destabilization of desert ecosystems in the Western United States.

Many of the larger and more intensively used military training lands in the United States occur in the Sonoran, Mojave, Chihuahuan and Great Basin desert ecosystems. The abundance, diversity, and population stability of the flora and fauna in those ecosystems are naturally limited. The stability of the soil matrix is largely dependent on microphytic soil crusts composed of tiny algae, fungi, bacteria and lichens that are adapted to the harsh conditions and occupy the top few millimeters of the soil. Many of these organisms form microscopic filaments and exude polysaccharide compounds that bind soil particles. The removal or destruction of these biological soil crusts by traffic, fire or pollution can accelerate soil erosion as much as 1500%.

Nutrient cycling in desert ecosystems is also intimately linked to microphytic soil crusts. Nitrogen-fixing cyanobacteria have recently been shown to be the primary source of nitrogen in at least some desert ecosystems. Plants grown in the presence of a microphytic soil crust have been found to have twice the biomass and twice the nutrient concentration compared to plants grown in the same soil without the crust. Based on this information, some scientists have speculated that the decline of the desert tortoise and the desert big-horned sheep may be linked to the decline of microphytic soil crusts, *i.e.*, these species suffer from a variety of malnutrition-related maladies despite an apparent abundance of preferred plant materials.

Despite the apparent critical nature of soil microphytes in desert ecosystem stability, surprisingly little is known about the physiological mechanisms that allow the organisms to perform specific ecosystem functions.

This is a new program arising from information derived from a previously funded basic research effort entitled "Hydrologic consequences of vehicular traffic on crusted soil."

This program supports the Conservation Pillar of the Tri-Service Strategic Environmental Research and Development Plan. Specifically, this effort is partial fulfillment of the program line entitled "Propagation of Cryptogamic Plants" on the Range/Training Area Revegetation roadmap.

### **Project Description:**

The research effort will concentrate primarily on the filamentous cyanobacterial genus *Microcoleus*, one of the most ubiquitous genera occurring in the arid ecosystems of the Western United States. Although nitrogen can be fixed only in anaerobic environments, this genus does not possess intracellular heterocysts to exclude oxygen. It is, nonetheless, one of



the dominant nitrogen fixing genera in desert soils. The mechanism of oxygen exclusion may be related to the development of extracellular polysaccharide sheaths. Using microprobes and acetylene-reduction assay, this research effort will seek to identify the exact mechanism of oxygen exclusion. Experiments will also be conducted to identify factors that promote the reproduction of filaments, that induce sheath production, and that determine the number of filaments per sheath.

The long-term ecological implications of the destruction of *Microcoleus* and other microphytes will be evaluated in the field by comparing the biomass and nutrient status of plants living in undisturbed areas with adjacent areas having a history of various intensities and durations of disturbance. Where possible, this will be linked to fluctuations in animal populations.

#### **Expected Payoffs:**

Basic information derived from this effort will improve our understanding of the long-term ecological implications of disturbing desert ecosystems. In addition, it is likely that an understanding of the physiological and reproductive processes of *Microcoleus* and other microphytic genera will help facilitate the restoration of fully functional arid ecosystems following disturbance.

Successful completion of this program will facilitate transition to other basic and applied research programs outlined within the Conservation Pillar roadmaps of the Tri-Service Environmental Strategic Research and Development Plan. Specifically, this project will transition into the basic research efforts entitled "Effects of Algal/Mycorrhizal Interactions on Ecosystem Stability" and "Ecosystem Structures/Processes and Species - Habitat Relationships" on the Range/Training Area Revegetation and Sensitive Ecosystem Management roadmaps, respectively. In addition, it transitions to the applied research effort entitled "Microbiotechnical Methods for Restoring and Maintaining Biodiversity" on the Range/Training Area Revegetation roadmap.

#### **Milestones:**

Determine method of oxygen exclusion by <i>Microcoleus</i>	FY93
Identify location for field analysis of historic crust damage	FY93
Professional journal article on method of oxygen exclusion	FY94
Evaluate parameters that induce filament production	FY94
Evaluate parameters that induce sheath formation	FY94
Evaluate parameters that control filament numbers per sheath	FY94
Evaluate implications of historic crust damage on N-fixation	FY94
Evaluate implications of historic crust damage on flora	FY94
Journal article on physiology of terrestrial <i>Microcoleus</i>	FY95
Correlate floral alterations to faunal population fluctuations	FY95
Journal article on ecological implications of microphyte damage	FY95

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
250	250

**Technical Contact:**

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**SERDP Thrust Area: Conservation**

**Title:** Development of Regional Guidelines for Evaluating and Managing T&E Species Habitats on DoD Lands

**Problem Statement:**

Consistent and reliable procedures are needed to evaluate T&E species habitats and manage available resources to provide optimal conditions for a variety of species. Although endangered species concerns are being addressed collectively at the Washington level, the individual service branches and installations are using various means and sources of information/expertise in an effort to solve local problems. Because of this, there is considerable duplication of effort among the installations, and methods for evaluation and monitoring are often inconsistent. The major goal of this work is to develop regional guidelines that would apply to all installations within defined geographic areas. This is a new project.

**Project Description:**

This project will emphasize a regionalized and habitat-based approach to T&E species management. Regions will be designated according to geographic location, major habitat types present, and potential for supporting populations of the same species. For each region, generic T&E species evaluation methods and management strategies will be developed that apply to all installations within that geographic boundary. Habitat requirements will be defined for each species (based on the existing literature and coordination with species experts from other agencies, universities, and private organizations), and management strategies will be developed that apply collectively to species with similar habitat requirements. For example, a habitat based approach to T&E species management in riparian zones of the Southwest would recommend methods that protect and improve the system for all T&E species that depend upon these corridors for survival (i.e., snag management, re-establishment of native plants, and buffer zone protection would benefit all species present). It is expected that approximately ten (10) major regions will be designated for development of management plans. The USAE Waterways Experiment Station (WES) and Construction Engineering (CERL) will share equally in the work. There will be extensive coordination with other Federal agencies, especially the U.S. Fish and Wildlife Service, USDA Forest Service, Bureau of Land Management, and National Marine Fisheries Service.

**Expected Payoff:**

Potential users include all DoD installations with known or potential population of T&E species. The development of regional guidelines would eliminate much of the present duplication of effort and would result in a significant cost savings over time. The credibility of DoD T&E species efforts would be improved by providing guidance on habitat evaluation and management techniques that are consistent within a defined geographic region.

**Milestones:**

Select species and habitats for evaluation	FY93
Define geographic regions based on geoecological criteria	FY93
Conduct background survey on T&E species	FY94
Assess habitat requirements for species of concern	FY94
Develop management strategies and associated techniques for T&E species	FY94
Develop prototype regional guidebook	FY95
Develop regional habitat evaluation and management guidelines for selected species	FY95

**Transition Plan:**

Following the development of regional guidelines for selected species, strategies and techniques should be tested for reliability and effectiveness at several installation demo sites. This will allow management techniques to be tailored to specific habitats subjected to different military activities. Regional workshops should also be held to transfer information to the field.

**Funding: (\$K)**

	FY93	FY94
WES	150	300
CERL	<u>150</u>	<u>300</u>
TOTAL	300	600

**Performers:**

USAE Waterways Experiment Station, Environmental Laboratory  
USAE Construction Engineering Research Laboratory  
Cooperative developments will be established with the U.S. Fish and Wildlife Service at USDA Forest Service.  
Other Federal and State agencies will also be involved.

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## **SERDP Thrust Area: Conservation**

**Title:** Methods for Propagation, Translocation, and Reestablishment of threatened and endangered species.

### **Problem Statement:**

The objective is to develop and evaluate methodologies to propagate threatened, endangered, and sensitive species. This work will help installation natural resource personnel effectively reestablish populations of threatened, endangered, and sensitive species in areas least likely to conflict with the military mission.

Our information on the location of threatened, endangered and sensitive plant species, although incomplete, is actively being compiled and delineated on maps. What we are beginning to see is an increase in the number of threatened, endangered, and sensitive species requiring protection. This trend is expected to continue at an alarming rate.

Many sensitive plant species and populations have biological requirements that lend themselves to being successfully propagated. This project offers positive visibility for the military to be part of a recovery team effort and a mechanism for relocating sensitive populations to less conflicting locations. This positive reenforcement will provide an opportunity to balance biological requirements with training requirements of the military.

This project is a new project, but it is a proposed work unit in the DoD Environmental Quality Strategic Plan, Conservation Pillar, T/E Species Management, Propagation, and Recovery Thrust (refer to T/E Species Management, Propagation, and Recovery Roadmap). This project is funded as an 896 project for the outyears (FY96-99), but this effort can be moved up in years and provide additional support to the T/E Species Management, Propagation, and Recovery Thrust.

This project will compare the traditional current methods and techniques available for propagating plants and research new methodologies for reestablishing threatened, endangered, and sensitive species.

### **Expected Payoffs:**

Potential transition opportunities: This unit will directly feed into the related work units on the T/E Species Management, Propagation, and Recovery roadmap. In particular, it will permit data to be collected concerning cost analysis for the Resource Allocation Decisions scheduled in 1996, and provide recovery input into the work unit titled Systematic Capabilities to Evaluate/track T/E Species Mitigation, Management and Recovery.

### **Milestones:**

Investigate, compare, evaluate current techniques	FY93
Research and evaluate new techniques	FY94
Product: Guidelines, by category, for propagation, translocation, and reestablishment	FY96

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
350	358

**Funding Break down (\$K)**

<b>TASK</b>	<b>1993</b>	<b>1994</b>
Task 1	250	100
Task 2	50	158
Task 3	50	100
Task 4	0	0
Task 5	0	0
Total	350	358

**Technical Point of Contact:**

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Natural Resource Management Team  
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**SERDP Thrust Area: Conservation**

**Title: LCTA/BCD Biological Diversity Sensitivity Analysis**

**Problem Statement:**

The goal of this project is to better understand and utilize the TNC (The Nature Conservancy) BCD (Biological Data System), expand the scope of ongoing LCTA/BCD Linkage Project (Legacy), and populate the TES (Threatened, Endangered and Sensitive) Species database with elements emulated from the State Heritage Programs.

The DA (Department of the Army) is responsible for stewardship of their large land holding. The lands have a broad diversity of habitats that are home to endangered species, areas of uniqueness or importance, and harbor irreplaceable resources.

To better comply with ESA (Endangered Species Act) the DA is currently working on answering biological and ecological questions more efficiently, managing information on an increasing number of species, and providing an up-to-date computerized information on candidate and listed species. This project will expand the scope of ongoing work to better able analyze and rank sites for biodiversity and sensitivity.

This project is a new project. It will help enhance two previously funded efforts-the Legacy funded LCTA/BCD effort to develop joint data elements for threatened and endangered species and the A896 project for Systems Development of the TES database. It is one of the core work units in the DoD Environmental Quality Strategic Plan, Conservation Pillar, Sensitive Ecosystems Management thrust (refer to Sensitive Ecosystem Management roadmap).

**Project Description:**

This new work unit will build upon previous efforts of the LCTA (Land Condition Trend Analysis) program, enhance the TES database development, and complement efforts of our threatened and Endangered species work groups.

In order to provide DA with a listing and inventory of special biological elements this project will develop and expand the current TES database with special biological elements known to occur on DA installations. These biological elements will consist of federal listed endangered, threatened, candidates species, species and natural communities of state and national concern.

Identify, provide guidance, and supply appropriate special biological elements for incorporation and expansion of the TES database.

The proposed project will enhance the DoD activities by 1) identifying and characterizing special biological elements, 2) improve information management, 3) improve ability to evaluate land capability and restrictions, and 4) provide input into evaluating and monitoring special biological elements.

The following tasks must be completed:

- 1) The cooperators shall prepare a written project management plan with proposed schedule, office involvement, and methods for accomplishing the statement of work. The cooperators will also provide written guidelines and scopes of work prior to initiating work and agree to a memorandum of understanding.
- 2) Research the current listing of the special biological elements determined present on selected DA bases.
- 3) Determination of information needs of DA users.

**Expected payoff:**

The US Army, Corps of Engineers, Navy, Air Force, and National Guard would find these products useful for managing their sensitive resources. Other government agencies, such as USDI BLM and USDA Forest Service, may also find applicability in the analysis. The TES program will provide information to those concerned with compliance or permitting and land use planning and scheduling.

A significant investment is being made in biological surveys for natural resources on DA lands. This project will better utilize these resources and information for a wider group of users to make more effective land use management decisions.

**Milestones:**

A significant investment of resources has been committed to natural resource monitoring programs. A standardized LCTA approach, compatible with state Heritage Programs for biodiversity sensitivity analysis, will allow for the DA to exchange information more easily and provide a more accurate information for land based decision making.

Projected accomplishments for the execution year:

Year 1:

- 1) Written project management plan with proposed schedule, office involvement, and methods for accomplishing the statement of work.
- 2) Written guidelines and scopes of work for biological diversity sensitivity analysis (i.e. field survey guidelines, field methodology, and cost analysis). If necessary develop the materials, guidelines, and identification of appropriate levels of information on biological data elements.
- 3). Conduct literature searches on sensitive species and sensitive habitat requirements for selected installations to provide detailed machine-readable information on species biology and community ecology, including their requirements, ranking, and threats.
- 4) Provide a machine-readable listing of special biological elements determined present on selected DA bases in various levels of detail.



**Funding: (\$K)**

	<b>FY93</b>
Task	
1	50
2	100
3	75
4	125
Total	350

**Performers:**

Natural Resource Management Team, Environmental Sustainment Laboratories, USACERL.

The Nature Conservancy, HQ, Science Division; Department of Conservation, Springfield, IL;  
TESI, Threatened & Endangered Species Information, Golden, Colorado

Planned cooperative development agreements: MOU/MOA with all cooperators.

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## **SERDP Thrust Area: Conservation**

### **Title: Fishing Enforcement/Stock Assessment and Marine Mammal Monitoring**

#### **Problem Statement:**

The goal is to apply the U.S. Navy Integrated Undersea Surveillance System (IUSS) capabilities to support the compliance of the High Seas Driftnet Fisheries Enforcement Act (Public Law 102-582) and other national treaty and maritime law enforcement requirements, and to monitor various species of marine mammals to contribute towards conservation and regulations compliance.

The organizations targeted to accomplish this project are the Department of Commerce, National Oceanographic and Atmospheric Administration (NOAA), and National Maritime Fisheries Service (NMFS). Additionally, the United States Coast Guard (USCG), Joint Oceanographic Institutions (JOI), Office of Naval Research (ONR), and the National Science Foundation (NSF) will act in concert on this project.

The U.S. Government has entered into a variety of treaties with foreign nations, and has established domestic laws and regulations that are motivated by interests to protect the oceanic environment and to ensure the existence of a long-term viable commercial fishing industry.

Because the oceans encompass an enormous volume, monitoring compliance of fishing treaties, laws, and regulations, and even determining the approximate magnitude of fishing stock in an area, poses a daunting problem. As a concrete example of current enforcement problems, the U.S. Coast Guard flies random patrols over the North Pacific in an attempt to detect driftnet fishing violations. The Coast Guard realizes this approach has significant limitations, but for the most part, air surveillance is the only technique available. The Coast Guard requires a broad area surveillance technique that can non-cooperatively detect and track fishing vessels. IUSS has that nascent capability and, over the last thirty-five years, has repeatedly demonstrated its effectiveness with thousands of anti-submarine patrols involving maritime aircraft and other assets.

In September 1992, a brief experiment was conducted to determine signal processing requirements. The timing of this experiment offered a convenient opportunity to monitor over thirty driftnet fishing vessels in the Pacific Ocean, to cue maritime aircraft to the derived locations, and to share information with the National Maritime Fisheries Service. The preliminary results of the Pacific Driftnet Experiment clearly indicate that IUSS can readily detect, track, and localize fishing vessels.

Fishing stock assessments are important from an ecological perspective as the "health" of ocean areas are concurrently derived. Additionally, the accurate determination of fishing stock has important regulatory implications since catch limits are based, to a substantial degree, on the best assessments of the available resource. Stock assessments are currently estimated by expensive, labor-intensive, and infrequent sampling in limited areas, and by analyzing reported catches. The combination of existing techniques with IUSS capabilities will undoubtedly result in more thoroughly, efficient, and accurately determined fishing

stock assessments. IUSS can contribute towards improved assessments by monitoring fishing vessel activity, and possibly natural "predators" such as sperm whales and orca, and perhaps the aggregate noise spectra associated with fish and crustaceans.

In the Western North Atlantic basin, a limited and preliminary test was initiated in November 1992 to evaluate the capabilities of IUSS to detect, localize, and track three whale species: Finback, Humpback, and Northern Right. A significant volume of data has been collected thus far, some of which is surprising and controversial to scientific investigators. This truly is the first glimpse of an ocean basin-wide, synoptic of marine mammals.

This proposed demonstration and technology transfer constitutes a new program for IUSS.

#### **Project Description:**

The technical objectives of this proposal are to recognize, analyze, record, track, and catalog the acoustic signatures of appropriate fishing vessels, fishing stocks, and marine mammals, on an ocean-basin scale. Also to exploit and extensively automate existing Inter-Array Processor (IAP), Low Frequency Analyzing and Recording (LOFAR), and related capabilities. Additional objectives are to apply neural net technology in the automation improvements, to provide accurate position information on potential violators to USCG/NMFS, and to optimize the measurement of noise spectra and their association to biologies.

There are simply too many fishing vessels and marine mammals to identify and track by the traditional, human-intensive methodologies established for the anti-submarine mission. A key component of this effort, then, is an early and vigorous emphasis on developing automated techniques for localization, tracking and identification of "targets" of interest. This will be accomplished by the development of improved (broadband) beamformers for the acoustic arrays, and by accelerated development of neural net processors. Analysts in the loop will ideally focus on verification of the neural net analysis and refinement of the training of the nets.

Vital to the progress in these dual uses of the IUSS is the installation of hardware specifically dedicated to these additional missions; the key pieces of gear and the key facilities have been identified.

The data from the acoustic arrays will be processed in a secure environment. Selected IUSS facilities will have joint watchstanders comprised of, for example, NMFS, USGS, and other agency personnel working on a regular basis alongside IUSS watchstanders. Using the customized hardware, these joint watch teams will generate operational reports on fishing vessel activity, fishing stock assessment, and marine mammal tracking information.

In addition, unprocessed sensor data will be recorded and archived for subsequent off-line scientific investigations. A central data Dual Use Analysis Center (DUAC) will be established; it will consist of classified work area with work stations, several archive servers, and a classified data base archive. The DUAC will serve as a massive archive and scientific clearing house of data and information derived from IUSS resources.

Specific tasks to accomplish this project include:

1. Signal Processing: Implement broadband beamformer, neural network processing, and beam-to-beam correlation processing. Tasked to NCCOSC Research and Development Activity (NRaD), ORINCON, Inc., and ENSCO.
2. Workstations: Procure and install workstation hardware and software. Install Dual Use Workstations (DUWS), NRL/NOAA Acoustic Monitoring Systems (AMS) and NRL Acquisition Workstations (NAWS) at Naval Ocean Processing Facility (NOPF), Dam Neck, VA; Naval Facility (NAVFAC) Whidbey Island, WA; NOPF Ford Island, HI; and at the DUAC. Tasked to Naval Research Laboratory and others.
3. Analysis: Analyze collected data and use the results to develop appropriate personnel training material, improve signal processing via software development and train neural nets. Tasked to Naval Research Laboratory and others.
4. Experiments/Aircraft Observations: Conduct observations using maritime patrol aircraft (P-3). Tasked to Navy and Naval Research Laboratory and others.

This proposal clearly embraces the spirit of the High Seas Driftnet Fisheries Enforcement Act (Public Law 102-582) which explicitly requires "the Secretary of Defense, the Secretary of Commerce, and 'whatever department the Coast Guard is operating in,' enter into agreement which will make more effective the enforcement of domestic laws and international agreements to conserve and manage the living marine resources of the United States."

DoD has had a long-term interest in understanding marine mammals, in particular how they communicate over long distances. DoC policy is to protect endangered species, marine mammals being among the most publicly visible. To achieve protection, adequate information on species populations and their distribution is vital. Surprisingly, the migration routes of certain endangered species (e.g., the Northern Right Whale) remain unknown. IUSS ensures nearly total coverage of populations and movements on an ocean-basin scale and also provides a means by which to analyze their long distance communications.

The objectives of this demonstration and technology transfer are not all that different than those objectives associated with IUSS' current and traditional mission. IUSS currently tracks submarines; it is proposed that IUSS technology be used to track fishing vessels, assist in fishing stock assessment, and track marine mammals.

#### **Expected Payoff:**

This project supports Congressionally-mandated tasking of the Secretaries of Defense, Commerce, and Transportation. Also, it precipitates improved capabilities to enforce international treaties which are of commercial and private benefit to U.S. citizens. Provides the cheapest, most efficient "bio-health" look into the ocean basins and creates a global, ocean basin-scale capability to continuously monitor marine mammal activity. Lastly, this project will improve capabilities to assess fishing stock.

**Milestones:**

The milestones of this project are to install software/hardware; obtain and process acoustic data for fishing vessels, fishing stock assessment, and certain marine mammal species; and to fully transition IUSS product capabilities to NOAA/NMFS.

**Transition Plan:**

Implementation of this proposal will undoubtedly result in a smooth and effective transition of IUSS technology to NOAA/NMFS and marine life monitoring interests in approximately three years. The U.S. Navy (CNO (N874) and COMSPAWARSYSCOM PD80), NMFS, NOAA, USCG, and the Department of Commerce are and will continue to coordinate activities in support of Public Law 102-582.

Industry has assumed IUSS production requirements for the past 35 years and will continue to do so.

**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
Signal Processing	800	1000
Workstations	500	350
Data Analysis	620	620
SEANET Communications and Archive	80	530
Total	2000	2500

**Performers:**

Department of Commerce (National Oceanographic and Atmospheric Administration (NOAA) and National Maritime Fisheries Service (NMFS)), United States Coast Guard (USCG), Joint Oceanographic Institutions (JOI), Office of Naval Research (ONR), and the National Science Foundation (NSF).

Industry will develop software algorithms and provide appropriate Workstation hardware.

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## **SERDP Thrust Area: Conservation**

**Title:** Use of Navy Expertise in Marine Mammal Health and Physiology for Environmental Conservation

### **Problem Statement:**

The effect of estuarine, coastal, and ocean pollution on the high-visibility upper food-chain predators, whales, dolphins, porpoises, is poorly understood. Information by which to gauge pollution effects is not available.

The goal of this project is to employ Navy capabilities and experience to enhance marine mammal conservation. Identify opportunities for the wider use of Navy expertise in marine mammal health and physiology. Develop information on baseline values on pollutants and disease. Employ specialized expertise and unique marine mammal collections and data base at the Naval Command Control and Ocean Surveillance Center, Research and Development Division, (NRaD) for improvement of knowledge of marine mammal biology to assist in marine mammal conservation and to provide a potential sensitive indicator of pollution and disease in the natural ocean environment.

Ocean pollution is a controversial subject. Some environmentalists and environmental scientists raise alarms that the ocean is dying and that ocean life is severely contaminated. They call for drastic action requiring major changes of great economic and potential tactical impact in the way we use the oceans for recreational, commercial, and defense purposes. On the other side of the issue are user groups, and their operators, as well as some scientists who doubt claims that humans have done severe damage to the oceans, bays, and harbors.

A major case in point is the controversy surrounding the great public attention related to the die-offs of dolphins on the east and gulf coasts of the U.S. in 1987-89, in the Persian Gulf in 1986, and on the coasts of France and Spain in 1990. In all of these incidents, pollution was initially blamed. The 1986 event was not investigated thoroughly enough to make any conclusions as to cause since only four of more than 500 dead animals were examined. The later die-offs were much more thoroughly studied and implicated natural toxins, extreme climatic conditions, or disease.

High levels of some pollutants were found in many of the dead dolphins. Some environmentalists and environmental scientists maintain that these toxic agents were indeed the underlying cause of the die-offs.

Dolphins are at the top of the ocean food chain. They consume mainly fish which in turn consume other organisms in a chain or web that begins with plant life photosynthesis. Dolphins are mammals just as humans are, they have a relatively long natural life-span of 25 or 30 years, and a high-energy life style that requires the consumption of great amounts of food. In light of these facts, some scientists suspect that these animals will concentrate existing pollutants in the food chain to a much greater extent than short lived or low-energy ocean animals.

As the varieties and quantities of environmental pollutants have increased worldwide in correlation with human activities, there has been growing concern regarding the accumulation of such compounds within natural ecosystems and the threat they may pose to the sometimes delicate balance of these systems (Tsubaki and Irukayama, 1977; Toufexis, 1988). An increasing number of animal species have now been shown to have incorporated such pollutants and, in some cases, detrimental effects have been suggested or demonstrated (Gilmartin et al., 1976; Helle et al., 1976 a,b; Murphy, 1986; Martineau et al., 1988; Hose et al., 1989).

Inhabitants of the marine environment, from invertebrates (such as squid and crustaceans) to fish and mammals, have been especially vulnerable since toxic wastes which find their way into the marine habitat (as industrial by-products, runoff, or as a part of waste management programs) often spread through the system either through the dissolving effects of the water itself or by transport through mobile species assimilating the toxin within the food web (Heynders, 1988).

Marine mammals feed high on the food chain and can serve as ultimate bioaccumulators of a variety of marine contaminants (Reijnders, 1988; Andre et al., 1991). Because these mammals tend to be long-lived and because such toxicants as heavy metals generally have lengthy half-lives in biological systems, accumulation can continue over several years, magnifying the levels and potential impacts of pollutants within animal tissues. Since virtually any marine species will have incorporated at least some contaminants, it is no longer a question of determining whether or not a species harbors contaminants, but rather of clarifying at what level such pollutants exist and in what quantities they can be tolerated before posing a health liability to their host.

However, the issue of harmful levels is complicated by numerous variables which must be recognized for realistic evaluations. There are not only many types of pollutant categories (such as heavy metals, organochlorines and petroleum hydrocarbons) but their respective behaviors within the body can vary with contaminant type and with animal species. Also, a given contaminant may occur in different molecular combinations. For example, mercury can be incorporated in elemental form or it may be complexed to various organic moieties, as in the formation, for example, of methylmercury which is much more toxic than elemental mercury in isolation (Andersen et al., 1987). Also, certain heavy metals interact so that the combined presence of some (such as mercury and selenium) will affect the severity of associated toxicities (Ohi et al., 1980). Various pesticides, though toxic, may become even more hazardous as they are metabolized into intermediary compounds while the body attempts to process them for elimination (Payne et al., 1987). This last effect is further complicated by the fact that specific degradation products will vary with animal species since species differ in the cellular enzyme systems available for processing the original toxin. The age of the animal is also a factor since older animals may, in some cases, have higher levels of contaminants due to lifelong accumulations. The sex of the animal and sexual cycle phases must also be considered. Certain contaminants (such as some heavy metals) may be transferred across the placenta to the fetus during gestation; other contaminants (such as pesticides) are mobilized from the female during lactation and transferred to her offspring through milk. Accordingly, a very young animal can actually have higher levels of some pollutants than the mother who is many years older (Wagemann et al., 1988). Further, feeding habits after weaning are relevant to a consideration of toxicant loading since specific

contaminant levels will be directly influenced by contaminants present in the prey species themselves. Finally, individual animals will have variable histories of toxicant exposure which will affect their particular pollutant burden. Once contaminant levels have been determined, assessments must be made regarding the origin of the compounds detected; that is, it is important that attempts be made to determine whether the contaminants are linked to natural occurrences within a particular habitat or whether they have been abnormally injected into the environment as the result of human activities. It is only through such evaluations that realistic corrective actions can be implemented to address ecosystem imbalances of anthropogenic origin. In some instances, apparently high levels of a pollutant may be found to stem from natural "background levels" of that compound. For example, while high levels of mercury were detected in tissues collected from stranded striped dolphin (*Stenella coeruleoalba*) off the Mediterranean coast of France, it was concluded by the authors that the mercury came from natural sources in the Mediterranean Sea basin rather than industrial sources in the region (Andre et al., 1991).

However, a recent flurry of dramatic die-offs among several marine mammal populations worldwide has triggered questions within the scientific community regarding possible links with human-powered alterations of marine systems. Significant mortalities have included harbor seals (*Phoca vitulina*) in the North and Baltic Seas (Osterhaus et al., 1990), the striped dolphin (*S. coeruleoalba*) in eastern North Atlantic and Mediterranean waters around France, Spain, and adjacent regions (Miller, per. comm.) and the Atlantic bottlenose dolphin (*Tursiops truncatus*) along the eastern coast of the United States (Geraci, 1989). Investigations surrounding these events have emphasized the complex nature of their occurrence and such etiologies as natural infectious agents, biological toxins and environmental contaminants or a combination of such factors are being examined as responsible agents (Kuehl et al., 1991). All have generated considerable interest in the degree to which higher vertebrates may serve to monitor the environmental health of world oceans.

The beluga whale (*Delphinapterus leucas*) has received increasing attention with respect to environmental contaminants. One population in particular, that of the St. Lawrence River and Estuary in Quebec, Canada, is now suspected to be severely impacted by a variety of industrial wastes which have been steadily discharged into its environment (Martineau et al., 1988; Muir et al., 1990). High levels of organic pollutants such as polychlorinated biphenyls (PCBs) and Mirex as well as heavy metals such as mercury have been found in the tissues of this population and considerable evidence is mounting that the health of the St. Lawrence population is being measurably threatened when compared to belugas in other Canadian regions. There is some concern that the entire St. Lawrence beluga population will not survive current degraded habitat conditions if circumstances are not quickly addressed.

During January and February, 1990, a dramatic increase in the numbers of stranded Atlantic bottlenose dolphins occurred along the Texas coast, with reports escalating approximately four times beyond those reported for these months in the previous year (Haubold and Barron, 1990; Miller, 1991 in prep.). The event began in January when 23 animals were found dead in East Matagorda Bay and continued with increased mortalities more generally distributed along the Texas coast. Low ambient temperatures produced a surface freeze for several days in East Matagorda Bay; subsequent impact on the dolphins' food supply is thought to have played a significant part in the focal mortality within the Bay (Miller, 1992). However, the continuation of elevated stranding events along other regions of the coast



remains a puzzle, complicating interpretations of the total event. Stranding levels were also high in March (though only twice the levels reported in March 1989). Tissues have been collected from all dolphins (23) recovered from Matagorda Bay (as well as from three others which stranded on the Gulf side of Matagorda Peninsula at the same time) and from 22 other dolphins necropsied during January, February and March, apart from the Matagorda event, representing all six stranding regions of the Texas coast (Sabine Pass, Galveston, Port O'Conner, Port Aransas, Corpus Christi and South Padre Island).

This project was identified in the Department of the Navy Environmental Strategic Plan in 1991. One listed objective was to "identify opportunities for the wider use of Navy expertise in marine mammal health, and physiology by the end of FY92." In response to a memorandum from ASN (I & E), a proposal very similar to this one was developed and submitted but not yet funded as of this date.

### **Project Description:**

The Navy Marine Mammal Program based at NRaD has developed special expertise in marine mammal health and physiology during the past 30 years. NRaD maintains 100 bottlenose dolphins with origins (1st or 2nd generation) in the Gulf of Mexico. The dolphins are of both sexes with a wide range of age from immature through mature, and aged animals. These dolphins were collected over the past 30 years or born during that time at NRaD. Though they are genetically similar to their wild relatives in the Gulf of Mexico, the Navy dolphins have been fed fish and squid from other sources, primarily from the North Pacific ocean. Therefore, the Navy dolphins constitute a good control group for comparing both direct environmental pollution and food-borne or food-web concentrated pollution.

The Navy conducts complete physical examinations at six-month intervals. Therefore, consistent health records are available on each individual which chronicle much medical and physiological information that can be used in the proposed study. The animals, the data base, and the special expertise at NRaD could be utilized to enrich the health of the marine environment through development of data and methods by which the natural populations of bottlenose dolphins, other marine mammals, and possibly other large marine species could be assessed. Wildlife management officials will have better information with which to formulate decisions about marine mammal conservation. Furthermore, this data will also have the potential to reveal sensitive bio-indicators by which the status of the ocean environment can be further evaluated.

The marine mammal data base on animal health and physiology at NRaD will be reviewed, analyzed and data published correlating values with biological characteristics of animals such as sex, morphometries, and age. Without the Navy records, only a small amount of these data is currently available. Serial measurements will be made of different blood and plasma components to determine which constituent offers the most consistent and reliable values in the assay for a selected list of pollutants and diseases. Serial measures will also be taken from blubber biopsies for correlation with the most consistent blood measures and with the same biological characteristics mentioned above. No additional animals will be required and no additional manipulation of marine mammals will be necessary for these studies. All of this information will be collected during procedures mandated under the health maintenance program. Numerous additional tests and modern procedures will be carried out with the

materials already collected from Navy marine mammals. Publication of this new information will serve as an invaluable reference for evaluating individuals in wild populations and especially will help in elucidating future die-off diagnosis and prospective courses of action. This data will also have the potential to identify ocean pollution as concentrated in marine mammals because it will provide the basis for comparison with similar data collected from animals from wild populations.

Department of the Navy Environmental Strategic Plan listed an objective as to identify opportunities for the wider use of Navy expertise in marine mammal health and physiology by the end of FY92." DOD past, perceived, and potential impacts on critical habitat and food chains in coastal and ocean environments used by dolphins are always a potential sensitive public issue when die-offs occur. Presently, the information does not exist to assess the role of pollution from any sources in these die-offs.

Accordingly there exists a tremendous need to conduct broad-spectrum probes. In this mammal group for a variety of potential environmental contaminants in the Gulf region. Monitoring such contaminants in marine mammal populations as ultimate pollutant bioaccumulators provides a window on the Gulf at the higher vertebrate level which serves to evaluate not only potential, health liabilities which may be operating within the marine mammals themselves but also provides an opportunity to index the health of the Gulf environment generally. Such an investigation will contribute to the process of defining specific pollutant study needs by revealing those contaminants requiring closer scrutiny. The project will lead to a better understanding of pollutant concentration in marine mammal populations within the Gulf of Mexico which can instruct future environmental study strategies seeking to evaluate human impacts within this heavily utilized marine ecosystem.

#### Tasks:

I. Database analysis. The existing database will be analyzed for physiological parameters relative to the project objectives.

II. Archive and Filed Specimen Collection. The following specimens and related data have been collected through the Texas Marine Mammal Stranding Network (TMMSN) and through necropsies conducted at NRaD in support of toxicologic studies: (1) Tissues for toxicological analysis - five tissue types (blubber, muscle, kidney, liver, bone) have generally been collected from each of the dolphins during necropsy. Attempts were made to collect all samples from the same basic location for each tissue type. (2) Teeth have been collected from stranded dolphins by removing the 8th tooth from the rear of each arcade or, alternatively, 3-4 teeth from the midportion of the left lower jaw. Age assessments will be made for these teeth. (3) History and other data have been recorded.

III. Laboratory Analysis. Heavy metal analyses will be performed on tissues varying in condition from very fresh to decomposed (condition codes 2-4) since elemental analysis will be unaffected by tissue condition. Samples will be slightly thawed to facilitate cutting and a titanium knife will be used to trim the edges of each tissue to eliminate any contamination that might have been introduced during field collection. Approximately 1 g of tissue will be placed in a Savillex teflon digestion bomb and digested with 3 ml ultrapure nitric acid for 8 hours at 120°C. The digested sample will be diluted with 20 ml of deionized distilled water

and transferred to a polyethylene screw-cap bottle for analysis. Because this is a wet tissue digest procedure, 2 g of tissue will be dried to a constant weight and percent dry weight calculated to facilitate comparisons with other data sets from the scientific literature where results may have been reported as dry weight values. Mercury concentration will be measured by cold-vapor atomic absorption spectrophotometry (AAS); the other six elements will be assayed by graphite furnace AAS. Organochlorine analyses will be limited to very fresh tissues (condition code 2 or better) since organic compounds begin to degrade as tissue decomposition proceeds. Approximately two grams of tissue will be weighed, minced and homogenized using a Tisumizer in a 50:50 mixture of dichloromethane-cyclohexane. The homogenized tissue sample will be weighed and allowed to come to constant weight for total lipid estimation. Dried dolphin tissue samples will be thoroughly mixed with 3 g Bondesil C18 using a glass mortar and pestle. The mixture will be loaded to the top of an acetonitrile washed column filled with a bottom layer of 10 cc of florosil and a top layer of 5 cc Bondesil C18. Chlorinated hydrocarbons and polyaromatic hydrocarbons will be eluted from the column with 15 ml of HPLC acetonitrile. The acetonitrile will be evaporated from the eluted mixture and the residue resuspended in 50 ml of methanol. Dilutions will be prepared from these stock resuspensions. The halogenated hydrocarbons will be identified and quantitated by gas chromatography/electron capture. The non-halogenated compounds will be identified and quantitated by either gas chromatography/ mass spectrometry or gas chromatography/ flame ionization.

Considerable care must be exercised in the evaluation of environmental contaminants found in marine mammal tissues since the determined levels are a function of numerous variables which must be considered if realistic assessments are to be made. There are not only several types of pollutant categories (such as heavy metals, organochlorines and petroleum hydrocarbons) but their respective behaviors within the body can vary with contaminant type and with animal species. Also, a given pollutant may occur in different molecular combinations. For example, mercury can be assimilated in elemental form or it may be complexed to various organic moieties, as in the formation, for example, of methylmercury which is much more toxic than uncomplexed elemental mercury (Andersen et al., 1987). Also, certain heavy metals interact, so that the combined presence of some (such as mercury and selenium) will alter the severity of associated toxicities (Ohi et al., 1980). As another example, various pesticides, though toxic, may become even more hazardous as they are broken into intermediary metabolic products while the body attempts to process them for elimination (Payne et al., 1987). This last effect is further complicated by the fact that specific degradation products will vary with animal species since species differ in the cellular enzyme systems available for processing the original toxin. The age of the animal is also a factor since older animals may, in some cases, have higher levels of contaminants due to lifelong accumulations. The sex of the animal and sexual cycle phases must also be considered. Certain contaminants (such as some heavy metals) may be transferred across the placenta to the fetus during gestation; other contaminants (such as pesticides) are mobilized from the female during lactation and transferred to her offspring through her milk. Because of this, the very young animal can actually have higher levels of some pollutants than the mother who is many years older (Wagernann et al., 1988). Further, feeding habits after weaning are central to a consideration of toxin loading of marine mammal systems since specific contaminant levels will be directly influenced by contaminants present in the prey species themselves. Also, individual animals will have variable histories which will affect their particular pollutant burden.

Because of these variables, the animals utilized in the current study will be limited to those for whom complimentary data (such as body morphometries, accurate estimations of age, sex, reproductive states are available. Geographic information will also be required of the animals in the study group, including specific location of stranding or site of capture for those animals used in the Navy program. All analyses will be run with control samples as detailed above to ensure accuracy of determined contaminant levels.

#### **Expected Payoff:**

More information and technology will be available for assessment of all human impacts, including DoD impacts on die-offs of dolphins in the coastal areas of the United States and elsewhere. Reports listing critical criteria will be distributed to stranding networks and cognizant government agencies at all levels.

#### **Milestones:**

Identify critical features of database	FY93
Correlate features with biological facts about whales and dolphins	FY93-94
Assemble archived tissues and new tissues	FY93-94
Identify collaborating laboratories	FY93-94
Packed cell and tissue specimen analysis	FY93-95
Physiological reports from database	FY93-94
Report on toxicological and health criteria	FY95
Distribute reports to stranding networks and user agencies	FY95

#### **Transition Plan:**

Marine mammal protection agencies at local, state and national level are identified. Volunteer stranding networks exist along most coastal areas of the United States. Information from this work will be distributed to these users as well as to the general scientific community.

#### **Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
249	409

#### **Performers:**

Navy Department, Naval Command Control and Ocean Surveillance Center, RDT&E Division (NRaD), Code 51.

Science Applications International, Marine Division through contract with NRaD.

The proposed investigation would be orchestrated through the combined efforts of several federal, state and private agencies, including the National Animal Disease Laboratory, Toxicology Branch (Ames, IA), the College of Veterinary Medicine (TAMU/CVM) and the Geochemical and Environmental Research Group (GERG) of Texas A&M University (College

Station, TX), the Department of Veterinary Pathology of the Armed Forces Institute of Pathology (AFIP) and possibly the Environmental Protection Agency (EPA), Northeast Center.

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## **SERDP Thrust Area: Conservation**

**Title:** Identification, Assessment, and Mitigation of Impacts of Military-Related Chemicals and Pollutants on Threatened and Endangered Species

### **Problem Statement:**

The goal is to determine the impacts of military-related chemicals and pollutants on threatened and endangered species and to apply this information to permit the maximum use of military lands for training and other purposes which will still protect threatened and endangered species as required by regulation.

The Endangered Species Act (ESA) protects threatened and endangered (T&E) species and critical habitats from all manner of biological, chemical, and physical impacts. In addition to physical impacts to species and their habitats resulting from military training, such species present on military lands may be exposed to a variety of chemical hazards from training as well as grounds maintenance --e.g., smokes and obscurants, CS agents, pesticides and herbicides. An evaluation of the potential for ESA violations from military-unique and other chemical hazards is needed.

This is a new project to address an unfunded requirement under the Tri-Services Environmental Quality Strategic Research and Development Plan, DoD Pillar #4, Conservation. The Requirement Thrust is Training/Testing Impact Analysis on T/E. The specific requirement is Impacts of Military-Related Chemicals and Pollutants on T&E Species.

### **Project Description:**

USACERL is currently evaluating impacts of military operations on T&E species and vice versa. USACERL also has inventoried, or is in the process of inventorying, T&E species on selected military lands. The U.S. Fish and Wildlife Service has conducted species-specific research on some T&E species, primarily on a few large, high-profile vertebrate species. Little work has been done to evaluate impacts of chemical hazards on T&E species.

The objective of this work is to (1) evaluate the range of potential chemical hazards likely to be faced by T&E species on military training areas, (2) assess the effects of the environmentally hazardous materials, (3) develop protocols for evaluating direct and indirect effects in the field, and (4) recommend mitigation/management procedures to protect T&E species from these hazards.

Documentation will be developed on those hazardous materials most likely to impact T&E species in the field on military lands. Emphasis will be placed on those materials used in conjunction with training activities, but use and potential impacts of other agents such as pesticides and herbicides will be evaluated as well. Protocols will be developed for conduct of direct field studies which will include evaluation of not only direct impacts on specific species but also indirect impacts likely through the food chain and habitat. Mitigation guidelines and methods will be identified to enhance protection of T&E species and their food and habitat resources.

This effort is intricately tied to the existing Tri-Services Environmental Quality Strategic Research and Development Plan, DoD Pillar #4, Conservation. The specific Requirement Thrust is Training/ Testing Impact Analysis on T/E. This proposed work meets DoD's objective for evaluating impacts of military-related chemicals on T&E species, and is related to similar projects designed to evaluate physical, biological, and sensory impacts of military operations on T&E species. The work also relates to DoE's research to develop field protocols for evaluation of chemical contamination impacts on the environment.

This investigation will enhance and compliment other ongoing or planned work by USACERL on T&E species on military lands, e.g., impacts of military activities on physical and biological characteristics of T&E species habitats, sensory impacts on T&E species from military activities. The proposed work is a critical link in scientifically evaluating impacts of military operations on T&E species. Results of these studies together will serve as a basis for selecting appropriate mitigation options to ensure long-term availability of training and testing lands.

Specific tasks for this study are:

Task 1. Identify potential hazards.

The first task is to evaluate the range of potential chemical hazards likely to be faced by T&E species on military lands. The chemicals used on military lands will be identified and information collected on areas and levels of use. Based on evaluation of this information, we will develop a list of hazardous chemicals and pollutants which are of concern.

Task 2. Assess potential effects.

This task is to assess the potential effects of the environmentally hazardous materials based on information on known characteristics and effects of the chemicals as well as the potential distribution in the environment. We will then compile descriptions of the potential effects of these hazards.

Task 3. Develop protocols for field studies.

We will develop and field test protocols for field studies to evaluate direct and indirect effects of the chemical hazards to T&E species on military lands. The protocols will be coordinated with current field methods development by the Subcommittee on Biological Field Methods of the Committee on Biological Effects and Environmental Fate (E47) of the American Society for Testing and Materials (ASTM). These protocols will address acute versus chronic effects and variations of habitats and regions. These protocols will be developed in coordination with the U.S. Fish and Wildlife Service and the Oak Ridge National Laboratory.

Task 4. Develop mitigation methods.

Appropriate mitigation and/or management procedures will be developed to protect T&E species from chemical hazards on military lands. Knowledge of the military mission as well as the ecological requirements of T&E species will be utilized to develop the procedures.

These procedures will thus permit maximum use of land for the military mission which will still protect T&E species as required by ESA.

**Expected Payoff:**

Potential users will be Army personnel who are responsible for protection of T&E species, for training activities, and for installation land management.

The results of this study will provide the capability to identify impacts on T&E from chemical hazards. Because the major impact from these hazards can often be delayed, it may be difficult to identify the cause in time to mitigate the effect unless a specific effort is made to identify the problem. Thus the capability provided by this study may prevent major effects to T&E species on military lands.

**Milestones:**

In the initial project year, we will (1) identify potential chemical hazards, (2) assess the potential effects of these hazards, and (3) begin to develop protocols for field studies.

FY93

Develop list of hazardous chemicals and pollutants of concern.  
Compile descriptions of potential effects of hazardous materials of concern.  
Initiate development of protocols for field studies.

FY94

Complete development of protocols for field studies.  
Initiate field tests.

FY95

Complete field tests.  
Complete development of mitigation/management methods.

**Transition Plan:**

Results of this study will be used in developing an Impact Monitoring System for T&E Species and in developing Guidelines for Evaluating the Impact of Military Operations on T&E Species (copy of chart attached).

The entire study will be closely coordinated with users. The program plan of which this study is a part has been developed with input from users. Users will be actively involved in providing information on military chemical use and T&E species occurrence and will be asked for input during development of field protocols and of mitigation/management methods. Site selection for field test studies and the conduct of those studies will be coordinated with appropriate Tri-Service partners. There will also be close coordination with those installations selected for field test studies.



**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
Tasks 1 and 2	525	
Task 3		750

**Performers:**

U.S. Army Corps of Engineers  
U.S. Army Construction Engineering Research Laboratories (USACERL)  
Champaign, IL

Interagency agreements are planned with the U.S. Fish and Wildlife Service and the Department of Energy, Oak Ridge National Laboratory to facilitate coordination and cooperative efforts under the proposed work.

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## **SERDP Thrust Area: Conservation**

**Title:** Application of Biomarkers for Monitoring and Assessment of Sensitive Fauna in Ecosystems Impacted by Munitions Waste and Defense Related Material Application Sites

### **Problem Statement:**

The goal of this project is to apply biomarkers (physiological, biochemical and molecular changes in aquatic and terrestrial organisms), as tools to assess and monitor impacts of defense-associated chemical production and applications, (e.g. munitions manufacturing, open detonation and open burning, decommissioning and de-arming chemical agents, fuel refining and storage, machine de-greasing wastes, and chemical by-products) on sensitive aquatic and terrestrial fauna at selected DoD facilities. Another goal is to establish patterns of biomarker changes, via comparative studies of native fauna in contaminated and reference sites, that are useful for demonstrating the existence or non-existence of ecosystem level impacts from these materials, and which appear to be predictive of decrements in the status of the ecological resources.

The U.S. Army has concerns about the potential ecological consequences associated with soil and water contamination by explosives, and the intermediates and by-products of explosives resulting from the synthesis and degradation (nitramines and nitroaromatic compounds) of these materials. The most common explosive nitramine pollutants are hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX); octahydro-1,3,5,7-tetranitro-1,3,5,6-tetrazocine (HMX). Among the nitroaromatic compounds, 2,4,6-trinitrotoluene (TNT) and several by-products are formed during TNT synthesis (dinitrotoluenes, trinitrobenzene and dinitrobenzene). In general, these products are degraded by microorganisms under anaerobic conditions but the consequences to ecological resources of exposure to these by-products (e.g., nitroso compounds) are unknown.

The development and implementation of environmentally responsible, cost-contained activities associated with defense operations requires relevant data for intelligent planning and preparation. Such data are generally not available and, as a result, the Army is often unable to conduct defensible, risk-based assessments of the potential impacts imparted by this class of ubiquitous chemicals to feral species and native plants in the vicinity of the affected DoD installations. Currently, DoD needs to initiate research for developing a quantitative data base for ecological assessments. This proposal will develop biochemical markers of exposure and effect on widely distributed and ecologically important species. These biomarker data will be evaluated, and the changes will be correlated with existing ecological resources in impacted and reference sites. The results will be used in a diagnostic mode to assess the impacts of the munitions contaminants, to prove or disprove the cause-effect relationships, and to guide clean up and restoration activities. This is a new project.

### **Project Description:**

The purpose of this proposed project is twofold: 1) to apply and validate, using readily available technology and expertise, an integrated matrix of biomarker endpoints for assessing exposure and effects of munitions-related contamination under laboratory and field settings, and 2) to evaluate the utility of this biomarker matrix as a tool for providing DoD with

advanced risk assessments of munitions-related contamination at the ecosystem level.

Site selection will be focused on those munitions-contaminated installation(s) which are located at a strategic proximity to ecologically appropriate reference site(s). The contaminated and reference sites will be inventoried and lists of ecological assets will be compiled. Suitable measurement endpoints will be selected on the basis of the biomarker methods available and on the ecological resources to be monitored. Assessments, based on the selected biomarker matrices, of exposure and effects from munitions compounds and by-products, on terrestrial and aquatic wildlife will be conducted. The biomarker profiles of selected wildlife will be compared in the contaminated and impacted sites and referenced against the status of the ecological assets. Biomarkers that appear useful as predictive of ecosystem impacts will be identified for future assessments at other DoD facilities.

Laboratory studies necessary to support the verification of field results will accompany the field studies. The laboratory studies will primarily focus on selected munitions compounds and their products (e.g., trinitrotoluene, trinitrobenzene, dinitrobenzene, tetryl and possibly the nitroamimes, RDX and HMX) dealt with in the field analysis.

Repeated measurements over time and across diverse landscapes will strengthen statistical ability to detect meaningful differences among populations within a study series. Site, species and specimen selection will be on the basis of the nature of the affecting agents, and will be conducted in collaboration with other investigators studying the site in terms of ecology, chemical contamination, and chronology of the overall impact. In addition, academic extramural resources and contractual service capabilities will be explored and utilized to expand critical components of the project. Examples of specific endpoints which can currently be utilized in these biomarker studies include:

- 1) Reproductive toxicology (e.g., computer assisted sperm motion analysis and flow cytometric characterization of spermatogenesis, sex hormone patterns, gonadal pathology, and developmental anomalies).
- 2) Molecular biology (e.g., the detection of genotype distributions within a population and losses of genetic diversity via polymerase chain reaction technology for DNA finger printing and electrophoretic allozyme frequency analysis).
- 3) Biochemical toxicology (e.g., quantitation of DNA and blood protein adducts, bile metabolites, and speciation of altered heme synthesis intermediates (porphyrins) as biomarkers of exposure to selected chemical classes; application of cDNA probes for detection of gene expression (e.g., cytochrome P4501a1), utilization of hepatic microsomal enzyme activities indicative of xenobiotic induction> (EROD, AHH, Glutathione S-transferase.)
- 4) Molecular histopathology (e.g., optical and electron micrography, in combination with computer-assisted image analysis and immunobased, pathology specific histochemistry).
- 5) Cellular and organ immunotoxicology (e.g., quantitative measure of phagocytosis and immune suppression, characterization and quantitation of oxidative burst capacity in phagocytic cells via laser activated fluorescence flow cytometry and cell sorting).

The Ecological Monitoring Research Division (EMRD) of the USEPA operates a modern, accredited animal research facility and is uniquely equipped and experienced in handling animal husbandry for a variety of terrestrial and aquatic species. The Division has developed breeding colonies of terrestrial (field mice, voles, and shrews, invertebrates, and plants), and aquatic (fish, tadpoles, invertebrates and plants) organisms. The division has state-of-art laboratory instrumentation as well as significant and proven experience in field sampling, sample preservation, transport and logistics. In addition, Division operates the USEPA Newtown Aquatic Facility with a wide range of aquatic ecotoxicological and bioassessment capabilities.

This research is innovative in two ways. Firstly, in an historically context, biologically derived information about ecological impacts have been limited to traditional evaluations of community structure and the direct measurement of chemical residues being dominant. Biological markers provide information not only to detect exposure but also to focus efforts where they are most needed for the protection of wildlife; namely, on contaminants that are biologically available, which bioaccumulate and which are biologically active (e.g., toxic). Secondly, the development and utilization of nonlethal and/or non-invasive sampling and measurement procedures have obvious advantageous as it would allow repeated sampling over time of the same marked individuals providing sequential temporal and spatial monitoring and will reduce sampling effects on the population studied (important for threatened or endangered species or small fragile populations) in the contaminated area.

This project will directly support the Conservation Strategy by providing quantitative indicators of the health status of the impacted fauna, leading to enhanced ecological risk assessment. The Department of the Army is in the process of establishing the toxicological and ecological data base for determining the potential environmental effects of munition chemicals that have been discharged in the environment over years. Currently, several on-going biomarker studies (in laboratory rodents) on 1,3,5-trinitrobenzene (TNB), 1,3-dinitrobenzene (DNE) and tetryl are being conducted in the EMRD.

Currently EMRD has an interagency agreement with U.S. Army Biomedical Research and Development Laboratory, Foet Detrick, MD to conduct studies on the adduction of nitroaromatic compounds with blood proteins and DNA as biomarkers of exposure. ENRD had developed sets of biomarkers in feral fish for the assessment of exposure and of effects industrial contaminants. These biomarkers have been compared to the fish community integrity via standard bioassessment metrics. Analogous biomarkers of mammalian reproductive toxicity have been developed and applied.

The technical issues to overcome include: the selection of appropriate site(s), and coordination with other research organizations dealing with the site studied; the selection, from appropriate existing or new biomarkers, those most appropriate for detection and assessment of exposure to munitions compounds, and, the development of systematic methods for using biomarker data to assess and predict ecosystem impacts.

**Expected Payoff:**

The proposed project will incur five major benefits to DoD (and the public):

- 1) It will provide baseline data to assess the ecological impact of munition activities, thus, it will assist in planning remedial intervention.
- 2) It will provide a quantitative means to document the ecological state of the impacted area and to prove or disprove cause-effect relationships between munitions byproducts contamination and ecological effects.
- 3) In terms of impact, (cost/time/efficiency/capability) it will provide means of documenting the cost effectiveness of ecological interventions.
- 4) It offers significant possible improvements in terms of timeliness of the ecological assessment process.
- 5) It will assist in evaluating/reestablishing genetic and biodiversity particularly of sensitive and endangered species at impacted area.

**Milestones:**

1993 to 1994: In collaboration with DoD: Conduct site(s) selection(s) (including appropriate site(s)), develop and finalize biomarker matrices (both for aquatic and terrestrial systems) determine appropriate research protocols and quality assurance issues, prepare plans for awarding cooperative agreements, interagency agreements and/or grants to perspective DoD and other US Government collaborators. Initiation Date 9/93; Completion date 6/94.

1994 to 1995: Finalize with DoD the study and reference site(s), conduct a peer review of the proposed protocol, initiate demonstration level pilots as appropriate, initiate as appropriate full scale field testing. Initiation date 6/94.

1995 to 1996: Complete data collection on initial study and reference site(s). Initiate data reduction and statistical analysis, initiate preparation (with DoD participation) of study peer review via a workshop presentation format. Prepare final conclusions/recommendations, and for peer reviewed publication of the results.

**Transition Plan:**

DoD/DOE will assist in the selection of priority site(s) for the study and for the chemical characterization of contamination agent(s) via a survey of prior DoD/DOE-funded and completed descriptive and analytical efforts. The target species will be identified in the impacted ecological community, and a control population will be identified at appropriate reference site(s). The testing chronology will be defined and coordinated with restoration activities. Biomarker matrix endpoints will be identified based on expected site impacts and via experience with previous industrial studies. In start-up phase validation of the sampling strategy, validation of assays, establishment of baseline reference ranges and quality assurance measures will be verified and reported to DoD. In the initial comparative phase

the sampling, assay data collection, and comparative analysis of impacted versus reference sites will be conducted and reported to DoD and the feedback will drive corrective action(s) in conformance with quality assurance standards. Finally, the evaluating phase will cover statistical analysis, peer review and preparation of a final report to DoD.

All of the above phases will require close consultation and coordination with DoD personnel in charge of the sites studied. Such communications will be both verbal as well as in the form of quarterly progress reports issued by the offeror.

**Funding: (\$K)**

FY93	FY94
900	900

**Performers:**

The scientific staff at the Ecological Monitoring Research Division (EMRD), Environmental Monitoring Systems Laboratory (EMSL), U.S. EPA have extensive training, hands on experience and expertise in the area of research that are required to carry out the proposed project successfully. They have a continuous record of peer reviewed publication in biomarker and ecological research. In addition, EMRD scientists propose to collaborate with scientists from the several DoD and US Government Facilities:

U.S. Army Biomedical Research and Development Laboratory, Fort Detrick, MD (DRS I. Baumel, G. Reddy, and H. Gardner);

US Fish and Wildlife Service Patuxent Wildlife research Center, Laurel, MD (Dr. N. Beyer);

US Fish and Wildlife Service Columbia Fisheries Laboratory, Columbia, MO (P. Baumann);

US Environmental Research Laboratory, Corvallis, OR (Dr. A. Fairbrother);

NIEHS Marine and Freshwater Biomedical Core Center for Great Lakes Studies, Milwaukee, WI (Dr. J. Lech);

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## Global Environmental Change

Project Title	Page Number	Funding FY93 (K)
Remote Sensing		
Joint DoD/DOE Atmospheric Remote Sensing and Assessment Program for Global Climate Change (DoD/DOE)	197	33,300
Acoustic Monitoring of Global Environmental Change (ARPA)	201	24,000
Definition and Demonstration of Remote Sensing Capability to Contribute to Environmental Understanding and Support for Environmental Issues (DSPO)	204	4,900
Environmental Task Force Research (DSPO)	208	2,000
Responsive Airborne Sensor Testbed for Environmental Research (Raster-J) (DSPO)	210	1,000
Data Manipulation Tools		
Strategic Environmental Distributed Active Archive Resources (N) *	216	5,000
Total		70,200

\* Congressional Interest Program



## **SERDP Thrust Area: Global Environmental Change**

**Title:** Joint DoD and DOE Atmospheric Remote Sensing and Assessment Program for Global Climate Change

### **Problem Statement:**

Global change of the earth's atmosphere is a critical environmental problem. Investigating, understanding and predicting climate change is the focus of a national effort. The measurements of these changes required to develop predictive models are obtained from existing and planned programs including NASA's EOS program. Unfortunately, the tempo of the development of satellite measurement capabilities is not keeping pace with the problem. This proposed SERDP project is to accelerate ongoing research and inject existing DoD/DOE sensor/satellite technology into the most critical gaps in the national program. The goal of this project is to investigate, understand and assess global atmospheric change by augmenting DoD space-based sensors for monitoring the middle and upper atmosphere and developing proposed DOE sensors for observing the troposphere.

Over the past ten years the Naval Research Laboratory (NRL) has made substantial investment and commitment to remote sensing of the middle and upper atmosphere. This includes the theoretical modeling effort needed to interpret the observations. This project will augment and focus specifically on the atmospheric global change problem and the development of an enhanced predictive capability. Our existing monitoring projects include a series of experiments to measure most of the important constituents of the middle and upper mesosphere, both neutral and ionized components. The middle and upper atmosphere observing program, by the addition of a UV imager for upper atmosphere remote sensing and a mid-latitude solar occultation stratospheric ozone monitor, complement our currently planned polar measurements.

### **Project Description:**

DOE is pursuing a program in Atmospheric Radiation Measurement (ARM) which is a major component of the United States Global Change Research Program developed by the Committee on Earth and Environmental Sciences (CEES). One of the goals of this program is to address climate change processes from the surface to the troposphere. This program consists of ground based and airborne instruments measuring lower atmospheric energy balance and cloud properties at several sites selected for their climatological importance. The aim of the ARM program is to gather data of necessary and unprecedented accuracy on cloud-climate feedback and earth radiation budget at the identified climatological sites.

The DOE portion of this project will be a complementary space segment to collect data on atmospheric processes at the ARM sites. This will assist the ARM objective to enhance the speed and reliability of improving climate predictability. Three sensors are proposed for this task: a Radiometric Imager, a Multispectral Pushbroom Imaging Radiometer and a Lidar for measuring cloud height. These instruments are candidates for flights on both air breathing and satellite platforms as available under the DoD's Space Test Program.

These instruments for the lower atmosphere will investigate the earth's radiation budget and

associated processes. This will give important information on the global tropospheric temperature and will allow an investigation of the poorly understood process of cloud feedback on the global warming problem.

In order to support this extensive measurement effort, a state-of-the-art data base system will be developed that will allow the data to be readily accessed and displayed. The data from the tropospheric sensors will be fully integrated with the ARM data system. The third leg of the proposed research effort is a theoretical modeling program. NRL currently has an operational 1-dimensional photochemical model of the middle atmosphere, and a 2-dimensional photochemical/dynamical model now under testing. We will augment this portion of the program by the addition of a 3-dimensional model which includes coupling between the lower, middle, and upper atmosphere and accurate orography to describe momentum transport and deposition in the upper atmosphere. DOE's ARM project has a similar modeling program for the troposphere. We plan to use the models in a synergistic fashion with the measurements. That is, the measurement will be used to test various model parameterizations and, thereby, improve these parameterizations. In turn, the models will be used to interpret the measurements. Through this combined program we hope to produce a large enhancement in the knowledge of the processes responsible for atmospheric global change and, thereby, an improved predictive capability.

Additional supercomputing capacity for this proposal and for the entire SERDP shall be provided from an existing facility which is geographically situated to provide the required staff necessary to ensure uninterrupted service. This facility will also be able to dedicate 13,000 central processing unit (CPU) hours of operational activity for an indefinite number of years in order to guarantee uninterrupted availability of the system. The system would have the capability of providing data management/data visualization technology, access to geographic information systems (GIS) methodology, as well as high speed computing capacity.

#### **Expected Payoff:**

This project should not be viewed as acting in isolation from other existing national programs to study global climate change currently in place at NASA and other CEES agencies. We have always worked very closely with these organizations and our work would be viewed as complementary. In particular, our remote sensing program is aimed predominantly at the 1995-2000 period. There is presently a great national need for space-based atmospheric measurements during this time period. The NASA Upper Atmospheric Research Satellite (UARS) was launched in September 1991 and has a total lifetime of 5-7 years. The next large-scale NASA space-based remote sensing program is the Earth Observing Satellite (EOS). EOS is not expected to be launched until at least 1998. Thus, there is a gap before the start-up of the NASA program which could be filled by our proposed program. Further, it is possible that a continuation of our program would complement the capabilities and global coverage of the large platform being considered by NASA. This would then allow an uninterrupted series of measurements of the sun/earth system for two decades which is required in order to sort out and understand the many complex and tangled issues involved in global change. In addition, our proposed program would put the DoD/DOE as equal partners with NASA and NOAA at the forefront of this vitally important research effort.

This project directly addresses the chemistry, dynamics, and variations of trace constituents in the middle and upper atmosphere. This plays a central role in several areas of DoD interest. Middle atmosphere: Longwave (VLF/ELF) communication systems, used for early warning and strategic communications, are dependent on the electron densities in the "C" and "D" regions of the ionosphere which are, in turn, controlled by the abundance of neutral middle atmospheric constituents. Among the most important of these are NO, H<sub>2</sub>O, and O<sub>3</sub>, all of which will be measured on a global basis by sensors proposed in this project. Also the natural variability of several trace constituents of the middle atmosphere, including CO<sub>2</sub>, H<sub>2</sub>O, and O<sub>3</sub>, is now the limiting factor in the performance of infrared space surveillance systems. Finally, neutral atmosphere density variations are critical factors which are needed for improved vehicle reentry and trajectory calculations. Upper Atmosphere: The upper atmosphere component of our project focuses on obtaining a suite of measurements which allows the characterization of the neutral atmosphere and the ionosphere above 100 km. The relevance for DoD of this region of the atmosphere is very similar to that listed above for the middle atmosphere. The "E" and "F" regions of the ionosphere are critically important in DoD communication and surveillance systems. In addition, neutral density variations, and their response to solar variations, are a necessary ingredient for calculating satellite drag.

#### **Milestones:**

Spaceflights for three stratospheric and ionospheric sensors.	FY93
Preliminary model evaluation using O <sub>3</sub> , NO, etc. Complete fabrication of tropospheric sensors. 3D dynamical/photochemical model incorporating gravity wave orography and climatology. Spaceflight for three atmospheric sensors.	FY94
Initial verification of atmospheric models. Spaceflight for tropospheric sensors (in cooperation with the CEES small satellite activity).	FY95
Spaceflights for five atmospheric sensors. Continued verification of 3D models.	FY96
Collection and analysis of data model. Confirmation of global climate change.	FY97-98

#### **Transition Plan:**

This project is a joint cooperative program between DoD and DOE, and should lead to further cooperation among NASA, NOAA, USGS, EPA, other Federal agencies, the university community and industry. The proposed program will be integrated into the CEES USGCRP via coordination with the Working Group on Global Change and its Task Groups. Opportunities for further collaborative efforts will be sought for optimum application of the federal research resources.

**Funding: (\$M)**

	<b>FY93</b>	<b>FY94</b>
NRL	8.3	7.1
DOE	25.0	9.5

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## **SERDP Thrust Area: Global Environmental Change**

### **Title: Acoustic Monitoring of Global Ocean Climate**

#### **Problem Statement:**

The objective is to conduct a "proof of concept" program to demonstrate the feasibility of conducting a long-term global program which will measure the temperature of the ocean and incorporate those measurements in appropriate climate models to quantify global climate variability. A demonstration system will be deployed in an ocean basin to gain experience for implementing a global system. At the conclusion of this effort it will be possible to make an informed decision on the establishment of a long-term (10-year) Acoustic Measurement Program to monitor climate variability.

Since ocean temperature is a key indicator of global temperature change, an accurate measurement of the temperature of the ocean would provide conclusive evidence of the existence and amplitude of global change. In the January, 1991, Heard Island Feasibility Test (HIFT) acoustic signals centered at 57 Hz were transmitted from the R/V Cory Chouest at a location near Heard Island (54 S, 74 E in the southern Indian Ocean) to 14 receiver stations manned by 9 nations. The paths between this source and the 14 receivers spanned all the world's oceans and extended to as long as 15,000 km. This test had two objectives: (1) Determine whether acoustic signals could be transmitted over global distances with modulated sources, and (2) Determine whether propagation times could be measured with the accuracy required for monitoring global warming. The HIFT was a success and demonstrated that acoustic signals of moderate intensity can be transmitted and received over global paths with sufficient signal to noise ratios to measure propagation time. In fact, signals at receivers in the Atlantic and Indian Oceans were received with signal-to-noise sometimes exceeding 40 dB. The arrival structure proved to be exceptionally phase-stable and persisted for 20 minutes to an hour, depending upon receiver location. Thus, the propagation times along the paths could easily be measured to the needed precision over time scales of this order. However, the HIFT data indicate that the multipath/mode structure of the arrivals is significantly more complicated than initially predicted. Interpreting these propagation-time measurements to infer average velocity along the paths is complicated by the effect of internal waves and mesoscale eddies. During the Heard Island Feasibility Test, marine mammal activity was monitored.

#### **Project Description:**

HIFT demonstrated the capability to measure propagation times over the very long paths needed to average out spatial variability. The next step is a more extended experiment to collect the data necessary to design the full-scale long-term program to measure global temperature changes. The major issues involve source and receiver design, resolution of the multipath/modal structure of the arrivals, and an understanding and quantification of the effects of natural variability of ocean temperatures. While HIFT demonstrated that available sources have adequate power, their reliability must be improved for long-term deployment. The initial approach is to deploy a moored, possibly directional, source at a 1 km depth operating near 70 Hz with a 20 Hz bandwidth. HIFT demonstrated that source levels can probably be reduced by 10-15 dB, and this plus the deep mooring will significantly reduce

the potential for adverse effects on marine mammals. To resolve the structure of the arrivals, both vertical and horizontal arrays are required. The plan is to use NAVFACs for the horizontal arrays and to deploy vertical arrays near some of the NAVFACs. While the simplest array configuration necessary to make the required measurements should be used for the long-term program, data from these more complex configurations is needed initially to understand the signals and their natural variability. For understanding the effects of seasonal and other natural variability, a deployment of at least 12 months is necessary. A modeling effort including both long-range acoustic propagation models and models for the ocean climate will be part of the program.

This effort will result in a demonstration program which will encompass sources and receiver arrays in the Atlantic and Pacific Ocean basins as well as the Arctic. The program will develop robust and affordable receiving stations, some of which might be vertical, horizontal, or three-dimensional arrays. Interconnection and networking of all data from the collection sites is a key element of the program.

The program is designed to develop the information needed for a FY94 decision on whether to proceed with the long-term program. This requires the collection, detailed analysis, and interpretation of large volumes of complex data in a short period of time. To accomplish this, the program will exploit advanced data collection, organization, and manipulation technologies developed by other DARPA programs. Also to be included is the initiation of arrangements for the transition of this "proof of concept" program from the development to the operational stages for an eventual long-term observation program.

This program will include academic performers, industrial partners, and government laboratories. Key academic performers will include: Scripps Institution of Oceanography, Applied Physics Laboratory, MIT, and the University of Michigan. Overall technical direction will be provided by Professor Walter Munk, the originator of this idea.

#### **Expected Payoff:**

This program will benefit the Office of the Oceanographer of the Navy by helping to resolve the issue of how to obtain and implement useful, affordable spatial maps to internal ocean variability. The emerging science of global acoustics will allow broad-ocean exploration and relates strongly to current Navy efforts, including the need for tomographic basin-scale mapping of ocean variability as an input to Navy ocean modeling and prediction systems. The results of monitoring of marine mammals around the experiments in this program will provide valuable scientific data for use in planning the long-term experiment.

#### **Milestones:**

Modify existing source	CY 92
Initiate source development	CY 92
Design and develop receivers	CY 93
Develop network design	CY 93
Initiate development of data collection systems	CY 92
Evaluate existing data	CY 92
Deploy source and receivers	CY 93

Establish data collection systems	CY 93
Collect data	CY 93
Monitor marine-mammal activity during experiments	CY 93
Evaluate results	CY 94
Decision point	CY 94

**Funding: (\$M)**

FY93	FY94
24.0	17.0

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## **SERDP Thrust Area: Global Environmental Change**

**Title:** Definition and Demonstration of Remote Sensing Capability to Contribute to Environmental Understanding and Support for Environmental Issues

### **Problem Statement:**

In order to better understand the dynamic environmental cycles that dictate our surroundings, it is essential to collect and analyze data in the most up to date and efficient manner. Data collection through remote sensing has been proven to be an ideal way to monitor environmental cycles as well to as create models in order to predict future environmental outcomes. The emphasis of this program will be to perform and analyze case studies, and to identify valid and specific applications for environmental sensing applications.

The goals of this project are to assess and enhance the potential for current space systems to contribute to solutions for environmental problems. Also to review and document archived data that is relevant to environmental issues. Lastly, to transfer technology and make the archived data reasonably available to the environmental community within acceptable security constraints.

Current understanding of the capabilities of remote sensing as they apply to national security issues infer that these same capabilities could provide data that would be of use to environmental research and regulation. The proposal leads to the investigation of this proposition and the documentation of the applicable data that responds to the requirements for environmental information. Further, this effort will examine enhancements that would improve the access to the data, systems, and the processes.

### **Project Description:**

The technical objectives are to provide a comprehensive listing of classified imagery holdings, along with a description of access procedures. Additional objectives include demonstrating the usefulness of the imagery archives to the environmental research community and demonstrating the utility of current classified remote sensing information to a sample of environmental problems. Lastly, improving cloud analysis models by developing algorithms that use all available meteorological satellite sensor information, as well as to establish a user friendly DMSP archive that is open to the general research community.

This proposal embodies the three general approaches of improving access to data, demonstrating environmental applications, and transitioning technology to the global change community. To improve data access the effort will include a survey of existing archives of classified data products and related database capabilities. The current archive and access procedures will be evaluated with respect to preserving the archive and allowing access by a wider community of users. Alternatives to existing procedures and policies which provide enhanced services will be investigated. In addition, the utility of selected data sets for supporting environmental applications will be demonstrated.

The Consortium for International Earth Science Information Network (CIESIN) will complement the above task by examining other unclassified DoD data (e.g. DMSP, arctic ice,



undersea, etc.), detailing its potential use by environmental users, and demonstrating prototype products and data retrieval services. The DMSP archive program will support access to cloud imagery, space environmental mission sensor data, and special mission sensor data (e.g. microwave sounder). Products will include inventory catalog for data and images, browse capability, and unique Environmental Data Records.

In demonstrating environmental applications, the areas of oceanographic, land, and atmospheric characterization will be studied. The task in oceanographic characterization is to access applications related to monitoring polar ice caps and glaciers to determine feasibility of mapping the ice edge, leads, and ridges within the sea ice pack, estimating ice thickness, monitoring the advance and retreat of glaciers, and studying the thermal mixing in coastal regions of the sea.

Land characterization would take the approach of assessing applications related to monitoring and managing environmental change and site characterization to support landscape characterization, identification of vegetation stress, detection and tracking of pollution and determination of other parameters which indicate environmental change. Lastly, the task of atmospheric characterization would be to examine use of classified information to improve analysis capability of cloud properties (type, coverage, radiance).

Presently the best, and for some cloud characteristics the only global cloud analysis is the Real-Time Nephanalysis (RTNEPH) residing at the U.S. Air Force Global Weather Center (AFGWC). RTNEPH became operational in 1983 and is based on mid-1970's technology. Current technology will be identified and applied to enhance RTNEPH capabilities and increase its access to the national and international climate modeling community. Algorithms will be developed to incorporate all available polar and geostationary meteorological satellites and their multispectral sensor information. Algorithms will transition to operational use at AFGWC, and will be made available to the civil sector. This task will also include identification of key analysis parameters and required architecture for an archive of cloud analysis data.

These efforts support the DoD/DOE SERDP objectives of improving data access, enhancing waste detection and restoration, improving analytical capabilities, and contributing technology and data to climate change research. This work also complements existing environmental work by focusing similar remote sensing techniques on previously untapped classified resources.

Previous efforts have focused on the exploitation of information for military and intelligence functions, some of which should be transferrable to environmental monitoring. Meteorological satellite information has been archived by agencies such as NOAA; however, these efforts have not included a systematic, easily retrievable, archive of data from all the sensors on the Defense Meteorological Satellite Program (DMSP). Previous cloud analysis modeling efforts have not fully incorporated all available polar orbiting and geostationary satellites.

#### **Expected Payoff:**

The inherent capability to provide non-intrusive data collection over significantly large areas

can enhance the ability of the environmental community to make accurate predictions of global change and environmental regulation monitoring. The extent of pollution may be promptly and accurately detected to speed assessment and policy formulation and the application of remediation technologies, as well as the development of more effective technologies.

The requirements for global cloud analysis and detailed representative cloud analysis and detailed representative cloud data have increased over the past decade. The need for increased access to cloud data and enhanced cloud analysis is critical and the components for developing it are available.

It is anticipated that this effort will lead to cooperation among DoD, DOE, NOAA, DoA, USGS, EPA, and other Federal Agencies. This effort promotes the establishment of a well defined process for accessing data and services that will enhance the mission accomplishment of Federal Agencies and improve the data available to the research community.

#### **Milestones:**

##### **Data Archive and Access:**

##### **DMSP Archives**

Image processing Software	Mar 93
Preliminary Product Assessment	Apr 93
Operational	Aug 93

##### **Classified Imagery Archives**

Complete Archive Survey report	Mar 93
Archive Analysis Report	Jun 93
Imagery Evaluation Examples	Nov 93
Prototype Products	Dec 93

##### **DoD Data Products for Global Change Research**

User Review	Feb 93
Data Acquisition and Reduction	Jul 93
Data configuration Established	Jul 93
Data Access Demonstration	Sep 93
Arctic Data Base Demonstration	Oct 93

##### **Demonstrations and Assessments of Classified Data and Systems (Oceanographic, Land and Atmospheric):**

Site Specific Test Plans	Mar 93 - Jun 93
Analysis of Existing Data	May 93 - Oct 93
New Data Collection	May 93 - Sep 93
Analysis	Sep 93 - Nov 93
Assessment and Findings	Oct 93 - Dec 93

##### **Technology Transfer:**

##### **Cloud Analysis and Archive**

User Survey and Initial Coordination  
Cloud Analysis Software and Hardware Specifications  
Cloud Analysis Algorithm Demonstrations  
Interagency Coordination  
Prototype Archive Demonstration

May 93  
Sep 93  
Oct 93-Apr 94  
May 93-Apr 94  
Apr 94

### **Transition Plan:**

The accomplishments of this work will transition in a variety of ways. The Imagery Archive, for example, will produce reference documentation pointing to the location and access procedures for all known imagery. CIESIN will demonstrate, for other DoD data sets, prototype access systems that can serve as models for future systems such as the Earth Observing System Data Information System (EOSDIS). The land, ocean, and atmospheric utility demonstrations will provide feasibility assessments for the use of classified systems in environmental monitoring and research. The results of these studies will be made available to policy-makers and potential users such as the Gore and Gates Environmental Task Force. The cloud analysis model algorithms are scheduled to transition to AFGWC's operational Cloud Depiction and Forecast System, a major acquisition funded for FY95 contract award. The DMSP Digital Archive task will produce an operation archive system, available to both federal and civil users, at NOAA's National Geophysics Data Center.

Classified activities are being reviewed by the Gore and Gates Environmental Task Force, a group of senior environmental researchers from academia and the nation's top research centers who have been granted special security accesses. Other activities such as the cloud analysis model and CIESIN will be presented in refereed journals and symposia. Where there is a technology transfer milestone, such as AFGWC, periodic joint program reviews are planned to ensure user involvement throughout the effort.

### **Funding: (\$K)**

FY93  
4900

### **Performers:**

Department and Agency Laboratory: Defense Support Project Office (DSPO), Naval Research Laboratory, DMSP Program Office, Air Force Phillips Laboratory, National Geophysics Data Center.

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**SERDP Thrust Area: Global Environmental Change**

**Title: Environmental Task Force (ETF) Research**

**Problem Statement:**

The Environmental Task Force was chartered by Mr. Robert Gates, Director of Central Intelligence, at the request of Senator Gore. The purpose of the ETF is to review classified data sets with the goal of determining which classified data could most help the scientific community address environmental issues. These issues include global climate change research, environmental restoration/monitoring, etc. The ETF is composed of an ETF steering committee for government management oversight, and the ETF science team for determining the usefulness of classified data for environmental issues.

The objective here is to fund research projects proposed by the ETF science team.

**Project Description:**

In January 1993, the ETF science team will complete an analysis of classified systems and data sets to determine which can be effectively applied against environmental issues and which cannot. It is almost certain that there will be some indeterminate "gray area" data sets whose value against environmental issues cannot be determined on the basis of currently available evidence. To help the ETF science team determine if these "gray area" data sets are useful or not, the science team will propose research projects to provide the necessary additional evidence.

It is expected that the majority of these projects will be in the \$100,000 to \$300,000 price range and no ETF project will cost \$1,000,000 or more. The maximum duration for any project will be six months.

By 1 February 1993, the chairman of the ETF science team will select and prioritize the most important projects, and then inform the ETF chairman and steering committee of the selection.

On 2 February 1993, the steering committee will recommend performing organizations for each of the projects. A science team member will be assigned to monitor each project. The ETF executive assistant has been assigned by the ETF chairman to manage the distribution of funds for the ETF research projects.

All ETF-related research will be completed on or before 2 August 1993 with a final report provided to the ETF science team chairman on that date.

**Expected Payoff:**

The results of the ETF research projects will help determine what classified data sets are useful for environmental issues and help the ETF science team complete their report on useful classified data.

**Milestones:**

FY93

ETF science team identifies potential research projects	Jan 93
ETF science team chairman identifies selected projects	Feb 93
ETF steering committee identifies performing agencies	Feb 93
Research projects initiated	Feb 93
Research complete and report forwarded to ETF science team chairman	Aug 93

**Funding: (\$K)**FY93  
2000**Performers:**

The performers of this research will be appropriately cleared government research laboratories and contractors. The selection of the performing agencies will be made by the ETF steering committee during February 1993.

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## **SERDP Thrust Area: Global Environmental Change**

**Title:** Responsive Airborne Sensor Testbed for Environmental Research - Joint Program (RASTER-J)

### **Problem Statement:**

No single sensor characterizes the environmental problem, and there is no current capability to provide near-simultaneous multi-sensor data collection for environmental research and applications. The goal of this project is a field demonstration of the utility and added value of simultaneous multi-sensor imaging for environmental phenomena and events, and transfer of DoD and DOE remote sensing technology to the environmental research community.

Analysis of environmental problems is frequently limited by a single "one dimensional" view of the scene of interest from a single sensor. Many of the basic environmental variables that are believed to be relevant to global climate change, such as soil moisture or snowpack content or net primary productivity, cannot be adequately described using single-sensor data sets. Indeed, this requirement for simultaneous multi-sensor data is one of the basic underpinnings of the Mission to Planet Earth (MTPE), and NASA's primary contribution to MTPE, the EOS satellite network. In addition, environmental insult events, such as oil and/or chemical spills, natural disasters and nuclear reactor meltdowns also demand the capabilities of multiple sensors and additionally have a highly critical response requirement. Immediate measures of the extent of environmental damage and the success of contaminant containment are vital.

Current and future global climate remote sensors also require calibration over a broad variety of terrestrial and oceanographic locations and features. No single sensor system is capable of providing calibration information for all of the sensors currently in space or being prepared for launch, and field studies to provide calibration are prohibitively expensive. Theorized sensors or combinations of sensors require testing to determine if they can improve the accuracy or sensitivity of environmental measurements.

The Naval Research Laboratory (NRL) is currently developing a high performance hyperspectral imagery sensor for civil and military applications under the HYDICE Dual Use Program. Seven civilian agencies DOE, EPA, USGS, NASA, USDA, USACE, and NOAA are HYDICE participants. From the hyperspectral view, the HYDICE program is addressing environmental requirements. The HYDICE sensor is a high performance imaging spectrometer that will be a substantial improvement over current instruments in the areas of spatial resolution, sensitivity, and radiometric calibration. Under this proposed project, the HYDICE C-141 platform will be populated with additional sensors to provide simultaneous data collection.

A core group of sensors have been identified, as well as a variety of possible subsidiary instruments. The HYDICE instrument would be the first element of the core. The second would be a millimeter-wave passive imaging system developed by NRL. This sensor is a multi-element 94 GHz radiometer providing spatial resolutions ranging from 3.6 to 30 meters, in swath widths ranging from 0.1 to 0.7 km, and with sensitivities in the range of 30 to 60 mK. Its imaging characteristics mesh well with those of HYDICE, and it appears to be

relatively easy to integrate into the C-141 platform. Among its intrinsic capabilities are determinations of ice type and snow age, measurements of soils moisture variations and wetland delineation, measurements of surface temperature variations, detection of forest fire hot spots and boundary lines, and oil spill detection and thickness measurements.

The third candidate core sensor is an advanced X-band synthetic aperture radar (ASAR), originally flown as part of the SR-71 Blackbird surveillance system. The fourth is a LIDAR. The initial plan is to work with a LIDAR contributed by DOE. However, NRL is building an Excimer pumped tunable dye laser whose spectral range (330 to 1100 nm) and rugged design (it is currently planned to be flown on a Navy P-3) would make it an ideal LIDAR system for this program.

### **Project Description:**

The technical objective of this project is to quantify the value added to current environmental remote sensing capability to be gained from the use of a responsive multi-sensor aircraft (RASTER-J). Current data products, collection techniques and distribution techniques will be evaluated. Exploitation algorithms and methods, concept of operations, tasking procedures, etc. will be developed. Besides DSPO sensors, other sensors to be evaluated as possible subsidiary instruments include a multi-spectral imager, advanced MWIR and LWIR imagers, ultraspectral sensors (using a standard FTS instrument, or perhaps a spatially-modulated transform device) and a standard stereo mapping camera. These sensors, primarily existing equipment, would provide complimentary data extending collections into regimes with higher spatial resolution and improved emissive IR sensitivity.

The sensor configuration will be defined to meet the technical and data exploitation objectives. The primary criterion of relevance to consideration status of hardware and software is beyond its potential environmental applications, and must include intrinsic instrumental parameters, instrumental parameters relevant to integration, matching operating characteristics to enhance mutual operation, and cost and schedule constraints. Issues critical to the utility of the testbed results, such as the degree of data coregistration achievable with the available sensors and platform, or the sensitivity mismatches imposed by driving sensors at a common V/H ratio, will be analyzed in detail. Aircraft integration plans and requirements will be defined, and sensor acquisition packages will be developed. Data collection requirements and processing, distribution, and archiving procedures will be developed.

Following program authorization and the second increment of funding, aircraft integration efforts will commence. The HYDICE C-141 test aircraft already has three separate camera wells and would require only minimal structural modifications. The spacious interior of the C-141 provides ample room for the installation of equipment racks to hold recorders and electronics associated with each sensor. In addition, timing, position, and orientation data, which is vital to the fusing of the multiple sensor data sets, are available in the aircraft. Integration will begin after the design phase is completed with data collection following that effort.

Parallel analyses and trade studies will be conducted to define the most effective sensor and platform combinations for future data collections and for implementation into an operational

multi-sensor platform which could respond to regional, nationwide, or even worldwide tasking to collect environmental data.

The science objective goal is to make DoD and DOE remote sensing technologies available for research into the extent, causes, and regional consequences of global climate change. The EOS plan calls for use of a wide range of instruments, including IR imagery, passive microwave and millimeter-wave imagery, SAR, multispectral and hyperspectral data, and LIDAR. An airborne platform equipped with an imaging spectrometer and passive millimeter-wavelength or SAR systems could provide the required spatial resolution and responsiveness. A key element of the global change problem is the determination of the ocean surface moisture and energy flux. This requires simultaneous measurements of the ocean surface temperature, the three-dimensional structure of the overlying water vapor and its motions, and precipitation; supporting data on the underlying currents and salinity would also be helpful. A platform combining an imaging spectrometer with sufficient spectral resolution and sensitivity to support inversion of the atmospheric water vapor profiles, and IR system for measuring sea surface temperature, a passive millimeter-wave system for determining precipitation as well as surface temperature, and a LIDAR to track atmospheric motions could provide detailed analyses of the full moisture/energy flux problem in targeted circumstances, and could support the development of algorithms to extract at least part of the information globally from satellite systems.

One of the most difficult sets of global change variables to measure is the cryospheric part of the hydrological cycle: snow albedo, snow water equivalent, grain size distributions, sea ice thickness, glacial morphological changes, and permafrost extent and seasonal melt. The synergistic combination of imaging spectrometer data with passive millimeter-wavelength data, SAR delineation of snow/ice/ground boundaries, and IR measurements of radiative fluxes would enable researchers to address some of these issues. The ability to bring radio as well as visible radiation sensors to bear is of particular importance, given the frequent heavy cloud cover in these regions.

It should be recognized that, while brought forward under the Global Change Thrust, RASTER-J has potential application to most of the SERDP thrust areas. True near-simultaneous multisensor observations have been discussed at length in the remote sensing community, but have proven difficult to accomplish. In lieu of operations on a common platform, field experiments have been conducted with joint participation by different individual aircraft. NASA put considerable effort into defining the requirements for simultaneous multi-sensor data to meet the global climate change problem as part of its justification for the Earth Observing System (EOS) program. Many of these broad programs—e.g., the need to obtain coincidental data on rapidly changing phenomena, the use of one sensor to solve data analysis problems. To a large extent, the differences between RASTER-J and EOS are just the differing capabilities and emphases of airborne and space borne instruments. The table following will illustrate:



	Spacecraft	Aircraft
Coverage	Global	Regional
Access	Global	Global with Restrictions
Resolution	Low	High
Revisit	Low	Continuous/As Desired
Time Scale	Long	Short
Duty Cycle	Limited	N/A
Tasking Time	Long	Short
Product Distribution	Slow	Near Real Time
Sensor Suite	Fixed	Flexible

EOS is intended to provide long-term global monitoring, and so emphasizes low to moderate spatial resolution observations at a fixed revisit rate. RASTER-J can provide much higher spatial resolution data, targeted to specific regions and opportunities. It is thus better for studying short term, irregular phenomena in highly structured regions. The sensitivities of EOS instruments are often limited by the altitude and velocity of orbital operations; the flight envelope of RASTER-J enables higher sensitivity observations, especially with the imaging spectrometer. The EOS instrument technology is now frozen; RASTER-J provides an engineering environment that supports an evolving, state-of-the-art sensor suite. Furthermore, our schedule puts RASTER-J in the field almost four years before the first EOS launch. The technical risks associated with this project are low. Existing sensors and those in advanced development will be incorporated into the multi-sensor aircraft. Candidate sensors to be included in this project will be evaluated for technical risk.

#### **Expected Payoff:**

This airborne sensor suite can be used to determine the value of simultaneously acquired data for environmental analysis. The improved measures of environmental conditions, phenomena, and events will significantly assist scientists in their efforts to measure and predict global climate change. Each sensor type has unique capabilities that can contribute to the overall accuracy and sensitivity of the measurements provided. The abilities of different sensors to image different aspects of an environmental events will allow the fused data sets to better describe environmental events which cannot be remotely sensed or are poorly understood at this time.

The RASTER-J system will provide calibration for current and future environmental sensors. The high degree of spectral and spatial resolution provided by these sensors will allow for the accurate calibration and algorithm calibration of ocean color systems such as SeaWifs over varied ocean areas at reduced costs over ground truth studies. The system will also allow for the more detailed study of specific vegetation species mortalities which may be associated with global climate change. Most global systems do not provide sufficient spatial and spectral resolution to study this phenomena.

RASTER-J will be capable of addressing many of the environmental problems confronting the DoD, DOE, and EPA. Contamination assessment, effectiveness of restoration efforts, compliance monitoring, hazards and risk assessment, and other tasks can be directly

assessed. The collected data will be of considerable value in developing strategies for pollution prevention by providing a detailed characterization of specific locales.

**Milestones:**

- Review current environmental data base; assess potential RASTER-J contributions.
- Initiate development of exploitation techniques and algorithms.
- Define concept of operations and tasking procedures.
- Define data collection, processing and distribution requirements and procedures.
- Define sensor configuration.
- Define sensor acquisition and integration requirements.

**Transition Plan:**

RASTER-J is a multi-user project exploring the synergistic value of merging multiple-sensor data for civil and military applications. Information gathered from this suite of sensors either individually or synergistically will spawn understanding and requirements and specifications for future airborne and spaceborne sensor designs. It will allow for phenomenology understanding for a broad set of environmental problems. RASTER-J will be the testbed for the regional fire truck concept advocated by many of the ETF participants. The transition of technology, data and exploitation algorithms exists for a myriad of users - State/local agencies, commercial, EPA, DOE, DOT, USDA, USGS, NASA EOS, etc.

**Funding: (\$K)**

	FY93
Task:	
1. Management/Operations Planning	100
2. System Performance Analysis	150
3. Sensor Trade Analysis/Architecture	150
4. Sensor Acquisition Planning	75
5. Aircraft Trade Analysis	100
6. Aircraft Integration Planning	175
7. Exploitation Techniques/Algorithm	125
8. Data Collection/Processing/Distribution & Archiving Planning	<u>125</u>
Total:	1000

Initial funding is approximately 6 person-years for the tasks shown below. Follow-on funding is contingent on the results of first year activities and on further program authorization.

**Performers:**

The plan is to build on the paradigm used for HYDICE - a joint service, well coordinated project. A RASTER-J project office will be established as the decision making body. This office will consist of NRL, joint service and technical support personnel. Collection and exploitation working groups will be set up involving participants from all interested agencies

and will be used as a basis of review, collaboration and requirements definition. Sensor integration and flight activities will be conducted by the USAF Air Material and Logistics Command.

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## **SERDP Thrust Area: Global Environmental Change**

**Title:** Strategic Environmental Distributed Active Archive Resources (SEDAAR)

### **Problem Statement:**

There is a diversity of environmental data and information which has been, and will be, generated through research and application efforts associated with global change and SERDP initiatives. Data and information contributors and users will include DoD and civilian participants. The potential contributions of these resources must be assessed and demonstrated. Additionally, technical capabilities must be demonstrated which will allow researchers to: (1) Identify relevant resources; (2) Identify data holdings; (3) Acquire data holdings, and; (4) Exploit retrieved data and information, generating value-added products supporting research and application efforts.

### **Project Description:**

The goals of the SEDAAR program are:

Demonstrate the value of relevant data. Emphasizing the value of relevant data obtained through networking with DoD, and non-DoD organizations. This includes raw data, processed data, metadata, and derived information products.

Demonstrate the value of relevant technologies. In order to obtain, exploit, and analyze relevant data, appropriate technical capabilities must be assembled and demonstrated.

Explore unique data product potential. Demonstrate the value of acquired data and information through the generation of value-added products.

The objectives of the SEDAAR program are: Assess the potential contribution of DoD data/information resources. This assessment is guided by application areas designated by research area specialists. Expedite data migration activities in the acquisition or, or access to, relevant data. Demonstrate data utility using current data/information interface, processing, and analysis technologies and techniques. This utility demonstration emphasizes the use of derived DoD data. Exploitation and analysis is conducted using a UNIX-based exploitation platform. Tools include a geographical information system (GIS), directory server, visualization tools, and user interface. Evaluate the process of data acquisition and exploitation. Evaluation of difficulties in obtaining sensitive data, adapting to various data formats and protocols, and assessing the usefulness of data acquired. Under FY 1992 SERDP funding the SEDAAR program is focused on the Arctic. Current SEDAAR activities emphasize the development and demonstration of an Arctic GIS and associated network support. FY93 SEDAAR funding will focus on expanding the data resources and use of network and application technologies. These efforts include:

Expansion of Data Sources and Resources. Current activity is focusing on migration of physical sea and ice data, derived from a variety of sources. FY93 funding will support activities to continue "synoptic coverage" of the Arctic, thereby building on the current effort. Data sources and resources will expand to diversify the data holdings and the application

areas addressed.

**Expansion of Application Areas.** Currently, Arctic research activities are the major focus of the SEDAAR program. FY93 funded activities will expand application areas to include:

**Comprehensive Arctic coverage** - continue the growth of data/information of physical characteristics of the Arctic. Expand data/information to include recent remotely sensed data as well as in situ data.

**Regional Applications** - Expand efforts to include subarctic coastal regions. Applications will emphasize data resources contributing to knowledge related to coastal geophysical processes as well as anthropogenic (human induced) impacts.

**Site Specific Characterization** - FY93 funded efforts will focus on supporting DoD site characterization efforts.

**Versatility of Tools.** The role of the SEDAAR tools is important. Utility demonstrations of the tools will continue and diversify under FY93 funding. Beta sites will be established.

SEDAAR activities started under FY92 funding will continue. These tasks include:

**Expansion of SEDAAR data holdings.** Holdings will continue to emphasize Arctic data resources. In addition, data and information contributions related to coastal global change phenomena will be captured. Continued emphasis on unclassified data sources, however, additional emphasis will be placed on deriving unclassified products from classified resources.

**Expansion of application areas.** Expand regional coverage to temperate regions (below 60 degrees N latitude) and specific target areas of interest to SERDP and global change communities. Application interest areas will diversify to include: 1) Land/sea interface phenomena; 2) Coastal environments and ecosystems, and; 3) Site specific environmental impact.

**Utility demonstrations of integrated technology.** Continue to demonstrate the utility of assessment/analysis tools implemented during FY92 funded effort. Emphasis technology areas include: (1) GIS; (2) Visualization, and; (3) Networking support.

#### **Expected Payoff:**

The SEDAAR program will expedite the release of DoD data and information resources to the global change community. Additionally, it will demonstrate technical and operational methods of acquiring and exploiting this data, in conjunction with other civilian data sources. The SEDAAR program will demonstrate as the usefulness of derived data to specific global change problems as well as SERDP-related activities.

**Milestones:**

Demonstration of initial SEDAAR (SEDAAR1) capability/ products	FY93
Release of data resource summary (SEDAAR1)	FY93
Beta installation of SEDAAR1 architecture/database	FY94
Completion/release of follow-on data resource summary	FY94
Demonstration of follow-on (SEDAAR2) capability/products	FY95
Dissemination of SEDAAR2 architecture/database	FY95

**Funding: (\$K)**

FY93  
5000

**Transition Plan:**

As noted above the initial SEDAAR (SEDAAR1) will transition to identified users (TBD) as beta capabilities. This transition includes tool architectures as well as populated databases. SEDAAR2 will also be transitioned in a similar manner.

**Performers:**

The SEDAAR effort will be managed by the ONR. Technical activities will be performed by CIESIN and its consortium member ERIM.

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## Installation Restoration

Project Title	Page Number	Funding FY93 (K)
Characterization, Monitoring and Related Data Bases		
National DoD Environmental Technology Demonstration Program (AF/A/N)	222	6,320
Advanced Fiber Optic-Based Spectroscopic Chemical Sensors for Cone Penetrometer (N)	229	425
Landfill Characterization System Technologies Demo at Kirtland AFB RB11 Mixed Waste Site (DOE)	234	620
Feasibility Study of an Environmental Technical Support Center (AF)	238	320
ECOTOX Data Base (EPA)	241	1,300
Consortium for Site Characterization Technology (EPA)	245	500
Fate and Transport Methods and Models Development		
Simulation of the Impacts of Subsurface Heterogeneities on Remediation Effectiveness (A)	249	4,310
Development of Military IRIS System for the Hazard Identification and Risk Assessment/Characterization of Defense Related Pollutants (EPA)	255	1,000
Toxicology and Human Health Risks (AF)	258	1,500
Fuels in Soils and Groundwater		
Enhanced Anaerobic Degradation of Jet Fuels in Groundwater (AF)	261	300
In Situ Aerobic Biodegradation of Hydrocarbon Fuels (AF)	264	400
Encapsulated or Immobilized Enzymes, Bacteria and Nutrients for Remediation of Fuel Spills (N)	268	350
Biodegradation Technology for Hazardous Waste Treatment (AF)	273	400
In Situ Treatment of JP-5 Unsaturated Soils (N)	276	950
Fuel Hydrocarbon Remediation (N)	279	895

Project Title	Page Number	Funding FY93 (K)
Solvents and Organics in Soils and Groundwater		
Field Research at Wurtsmith AFB (EPA)	283	1,000
Organophilic Clay Biosorption Treatment of Low Level Plasticizers and Solvents Contaminated Groundwater (A)	288	500
Treatment of Process Off-Gases Contaminated with TCE Using In-Situ Soil Based Aerobic Bioreactors (EPA)	294	310
PCB Decontamination Using Base Catalyzed Decomposition Process (N)	298	400
Demonstration of Enhanced Source Removal for Aquifer Restoration (EPA)	300	2,200
In-Situ Abiotic Degradation of Solvent Contaminated Groundwater (AF)	305	700
Air Sparging and In-Situ Bioremediation Integrated Project Demonstration at Picatinny Arsenal, NJ (A)	307	557
Groundwater Cleanup of Organic Contaminants (TCE/PCE) Using Methanotrophic Bioreactors (DOE)	311	1,650
Evaluation of the Semipermeable Membrane Device (SPMD) as a Passive In-Situ Concentrator of Military Organic Chemicals in Water (A)	316	50
Enhancing Bioremediation Processes in Cold Regions (A)	318	500
Heavy Metals in Soils, Sludges, Sediments and Water		
In-Situ Immobilization of Heavy Metals in Apatitic Minerals Formation (DOE)	321	350
Physical Separation Processes for Metal Contaminated Soils (A)	325	600
Energetics in Soils and Groundwater		
Peroxone Treatment of Explosives Contaminated Groundwater (A)	329	570
Applied Demonstration Program in Environmental Compliance and Bioremediation Technology (A) *	337	3,500
Structures Decontamination		
Field Demonstration: Use of Hot Gas Technology to Decontaminate Excavated Underground Piping (A)	340	670



Project Title	Page Number	Funding FY93 (K)
Application of the Base Catalyzed Dechlorination Process to Dechlorination of PCB Found on Navy Ships (EPA)	344	400
Total		33,547

\* Congressional Interest Program

## **SERDP Thrust Area: Installation Restoration**

**Title:** National DoD Environmental Technology Demonstration Program

### **Problem Statement:**

The recent emphasis placed on expediting remediation efforts of DoD/DOE facilities has likewise encouraged the development of novel remediation technologies. Unfortunately, their accomplishments have not been efficiently, nor effectively, transitioned to other technologists and the users within other agencies and the private sector. Inconsistencies in the conduct of site characterization, data collection and assessment, and incomplete dissemination of the attributes and value of the development have all contributed to this inefficient process. The National DoD Environmental Technology Demonstration Program (NETDP) proposal offers a alternative to help reduce the duplication of effort and inefficiencies associated with the current system and promote rapid transfer of technology to field applications.

In 1990, the Services developed and implemented Project Reliance, a coordinating technology program development and execution mechanism that supports non-Service-specific technology under a series of bi- and multi-lateral agreements. These agreements focus on the objective of promoting and enforcing joint or cooperative technology development in response to requirements generated from more than one Service.

The NETDP uses the Reliance agreements as its foundation. It focuses on the demonstration of remediation technologies that respond to the primary needs of the Services. As the principal manufacturer of field weapons, the Army has been given the lead in the area of energetics materials remediation technology, and the Navy and Air Force have been given primary responsibility for technology development in the area of petroleum, oils, lubricants (POL) and solvents. Each development task is conducted within this Reliance framework which is subordinate to the Environmental Quality Technology Panel under the Joint Engineers coordinating committee.

Under Reliance and the Environmental Quality Technology Panel, an Environmental Quality Strategic Research and Development Plan, known as the "green book", has been developed. Drafts of this document have been distributed to the SAB. It provides current details on the state-of-the-art of each technology development within the Environmental Quality area of interest and how they directly respond to the requirements as stated by the "user" community. All demonstrations currently proposed and planned are found in the technology development roadmaps contained in the green book and will be the planning document to be used for scheduling the demonstrations to be conducted at the selected and future demonstration sites.

While Reliance has provided a coordinating mechanism for the conduct of remediation technology development, it has not yet provided the support necessary to bring together technologies for side-by-side comparison, standardization of data collection and analysis, and publication of user guides and engineering design specifications. The Tri-Service NETDP proposal has this objective in mind and SERDP funds are proposed to achieve this objective.

## **Project Description:**

It has been determined that a minimum of five sites will be required to initiate demonstrations in the near-term. These five sites are based on the: contaminant of interest (energetics, fuels, solvents, heavy metals); media (soil or groundwater); and variability of soil conditions and types of contaminants. At this time, two sites (not yet determined) are required to conduct demonstrations focused on energetics contamination in soils and groundwater, one site (Port Hueneme Naval Facility) will focus on fuels, one (McClellan AFB) on chlorinated solvents and heavy metals, and another (Wurtsmith AFB) on petroleum hydrocarbons, PCBs, pesticides and dioxins. An additional sixth site is being planned by the Air Force to study the migration of contaminants in soil under controlled conditions. While the location of this site is yet to be determined, funds are required to assess potential sites through partial characterization.

While sites have yet to be chosen to demonstrate energetics technologies, a "short-list" is available and includes:

- Joliet Army Ammunition Plant (AAP), Illinois
- Volunteer AAP, Tennessee
- Milan AAP, Tennessee
- Cornhusker AAP, Nebraska
- Mississippi AAP
- Alabama AAP
- Lonestar AAP, Texas

The energetics and controlled release site selection process will continue upon approval of this proposal and will use the site selection criteria described below.

### SITE SELECTION CRITERIA

#### MEDIA TYPE

- Soil characteristics
  - Relative amounts of sand, clay, or organic matter
- Hydro/geologic conditions
  - Surface water sources
  - Ground water table
- Contaminants
  - Type of contaminants present
  - Concentration of contaminants
  - Depth and spatial profile of contaminants
  - volume of contaminated soil/subsurface

#### SITE SUPPORT

- Site accessibility
  - Near major transportation hub
  - Adequate road network

Site support facilities

Available and accessible utilities

Support from DEH or comparable organization

Laboratory and personnel support facilities

Site availability

Adequate size to conduct multiple demonstrations

Site not destined for immediate or near-term closure

**OTHER CRITERIA**

Impact on host facility

Potential for site expansion

Weather conditions

Impact on local population

Impact on environment

Regulatory acceptance

Available funding

**Tasks:**

- 1) List potential sites and select (more than one installation may be required to provide all appropriate testing conditions).
- 2) Establish technology selection oversight board. Membership will consist of SERDP participants, DoD, DOE, EPA, and other government agencies and private sector.
- 3) Identify potential technologies and select most efficient and cost effective candidates.
- 4) Develop management and demonstration plans.
- 5) Develop safety and standard operating procedures.
- 6) Obtain regulatory and research and development and demonstration permits.
- 7) Evaluate demonstrations, identify technology capabilities.
- 8) Prepare environmental impact statement if required.
- 9) Provide fabrication and procurement guidance.
- 10) Engage in technology transfer efforts to disseminate information resulting from demonstrations.

**Funding:**

Analysis of demonstration costs reveals that start-up costs for a "typical" demonstration site are approximately \$1,950,000. Requirements that are included in this cost are:

- obtain and analyze initial and ongoing characterization data
- evaluate and select test site
- preparation of the management, test and safety plans
- preparation of the NEPA documentation, to include RD&D permits and EIS
- provide project management and staffing
- instrumentation, facility construction and maintenance, and lab equipment purchase

As a rule of thumb, start-up costs are directly proportional to the complexity of the substrate and the area/volume that needs characterization. Furthermore, in the conduct of similar or related, past or present demonstration efforts at the recommended sites, each Service has

coincidentally fulfilled some, but not all of the above requirements. Consequently, the estimated, site-specific start-up costs vary from \$300,000 to \$3,100,000. See attachment B.

Collectively, the cost to initiate the five demonstration sites and the controlled release site totals \$9,070,000. However, several demonstrations are recommended to commence this year on several of the selected sites using SERDP funds. Part of the requested funds are for site management and preparation, and consequently, eliminating this double counting results in an initial cost savings to the FY 93 program. By deferring all site preparation and 50% management costs as defined in each demonstration proposal toward initial site development, a cost savings of \$2,750,000 is potentially realized; \$6,320,000 is now required to start these five sites and the additional controlled release site in addition to the funds provided for demonstrations that are scheduled to take place on these sites. Included in this figure are also site preparation and management costs for Wurtsmith AFB (\$3,100,000) and McClellan AFB (\$700,000) estimated by Air Force planners when developing this proposal. These costs were extracted, wholly or partially, from basic demonstration proposals during the Service review and incorporated into the NETDP.

#### FY 93 SITE START-UP COSTS

<u>Energetics Testbed</u> (2 sites TBD)		<u>\$000</u>
- Evaluate and select test sites		150
- Site characterization (data for monitoring well installation/maintenance*; soil sampling/analysis)		2,000
- Site use management plan		300
- Demonstration test plan and safety plan		300
- Regulatory and RD&D permits		400
- NEPA documentation/EIS		400
- Site staffing/project management		<u>320</u>
	Subtotal	3,870
 <u>Fuels and Solvents Testbed</u> (4 sites; 1 site TBD)		
<u>Wurtsmith AFB</u>		
- Site staffing/project management		600
- Facility development/maintenance (lab establishment/instrumentation)		1,500
- Site characterization (data for monitoring well installation/maintenance*; soil sampling/analysis)		1,000
<u>McClellan AFB</u>		
- Site preparation		500
- Site staffing/project management		200
<u>Port Hueneme</u>		
- Site preparation		300
<u>Controlled Release Site</u> (TBD)		
- Site characterization (geology and hydrology data for final site selection)		800

- NEPA documentation/EIS	100
- Demonstration test plan and safety plan	<u>200</u>
Subtotal	5,200

TOTAL START-UP COSTS 9,070

\* Calculated @ \$10,000 per well

POTENTIAL ECONOMIES REALIZED USING RECOMMENDED  
FY 93 DEMONSTRATIONS ON SELECTED SITES

Recommended FY 93 Project (Value \$000)	Identified Costs (\$000) for:		
	Site Prep	Mngmt (50%)	Total Costs
In-Situ Aerobic Biodegradation of Hydrocarbon Fuels	140	20	160
Demonstration of Enhanced Source Removal for Aquifer Restoration	1,800	150	1,950
Fuel Hydrocarbon Remediation	500	140	640
TOTAL	2,440	310	2,750

Total Start-up Cost Requirement	\$9,070K
Projected Economies	<u>\$2,750K</u>

Total Requested Funds for National Environmental Technology Demonstration Program	\$6,320K
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For future years, funding is required to maintain the sites and provide for data collection, analysis and distribution. A requirement may develop to identify additional sites, as defined by the Reliance mechanism and the EQ Strategic Plan. Separate funding requests for these sites will occur as necessary through the SERDP funding approval process. Outyear technology demonstrations will be based on the timelines outlined in the "Green Book" as modified by actual success of the technology development. As a technology development prepares for demonstration, direct liaison with the demonstration site management team is required to facilitate planning, scheduling and cost estimates for proposal development. This proposal would be subjected to the SERDP proposal selection process and determination made based upon its ability to respond to established selection criteria.

**Expected Payoff:**

Research pertaining to the development of technologies addressing energetic contamination is of a primary concern to many DoD representatives. This program would expand upon

current tri-service cooperative efforts and encourage participation with other government agencies and the public and private sector. The National Test Site Program will allow for the performance of comparative technology demonstrations, as well as, promote the development and evaluation of more cost effective technologies to address energetic contamination problems.

#### **Milestones:**

The proposed schedule of tasks to obtain approval, identify sites, obtain demonstration operation approval, and preparation of the sites is as follows:

##### **FY 93**

- SERDP Proposal Preparation, review and approval;
- Evaluate potential sites and select;
- Select technology selection/oversight board members;
- Obtain site characterization data;
- Prepare a management plan for site use;
- Develop test and safety plans;
- obtain regulatory and research and development and demonstration permits;
- Prepare environmental impact statement if required;

##### **FY 94**

- Develop technology demonstration plans;
- Prepare site for technology demonstrations, install and assemble equipment;
- Select test site management team;
- Start technology demonstrations;
- Initiate required contracts;
- Complete reports and cost analysis for demonstrated technologies to be used for technology transfer;
- Prepare fabrication and procurement guidance documentation.

##### **FY 95**

- Begin additional technology demonstrations;
- Evaluate feasibility of demonstrated technologies;
- Prepare report and cost analysis;
- Prepare fabrication and procurement guidance documentation.

##### **FY 96**

- Begin additional technology demonstrations;
- Evaluate feasibility of demonstrated technologies;
- Prepare report and cost analysis;
- Prepare fabrication and procurement guidance documentation.

**Transition Plan:**

Technologies selected for demonstration will offer the highest potential for technical success, economic effectiveness, as well as, transition to other federal agencies including both the private and public sectors. Early and extensive participation by the National DoD Technology Demonstration Sites Program members with each other and required regulatory agencies are essential to the success of this program. This cooperative participation will expand on current individual efforts leading to increased technical capabilities.

**Performers:**

In addition to DoD, DOE, and EPA, other principal partners in this initiative will be other federal agencies and services, as well as, both public and private sectors. In cooperation with the Deputy Undersecretary of Defense for Environmental Security, the SERDP Executive Director will provide program oversight. The technology selection and oversight board will consist of members from both the user and developer communities. On site execution and day to day oversight will be preformed by private firm contractors and/or other government agencies.

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## **SERDP Thrust Area: Installation Restoration**

**Title:** Advanced Fiber Optic-Based Spectroscopic Chemical Sensors for Cone Penetrometer

### **Problem Statement:**

The goal of this project is to develop and characterize spectroscopic-based optical fiber chemical sensors for use as in situ sensors with the cone penetrometer system. This will provide a capability for rapid subsurface screening of hazardous waste sites in order to greatly reduce the cost of site investigations and provide a means of tracking the progress and effectiveness of remediation efforts.

There is a need for rapid and cost effective methods for measuring subsurface distributions of chemical contaminants at DoD hazardous waste sites. At present it is necessary to drill monitoring wells and send samples to the laboratory for analysis. This method is slow, costly and provides poor spatial coverage. Results from the Army-Navy-Air Force SCAPS (Site Characterization and Analysis Penetrometer System) Program have demonstrated the feasibility of using a cone penetrometer system for pushing in situ sensors into the ground in order to map the subsurface distribution of chemical contaminants in order to guide placement of monitoring wells and to monitor the effectiveness of remediation procedures. At present the only sensor that has been demonstrated is the NRaD developed fiber optic POL (petroleum-oil-lubricant) sensor. Other sensors need to be developed to extend the capability to other contaminants of concern to the Navy (eg., benzene, toluene, xylene, carbon tetrachloride, trichloroethylene, heavy metals, explosives, etc.).

This proposal will enhance and expand the DERA/SERDP (Phase I) funded program at NRaD for development of fiber optic chemical sensors for use with the cone penetrometer system. The present program provides funds for addressing calibration issues related to the present fluorescence based POL sensor and some start up funds for a Raman based chemical sensor. Funds requested via this proposal will accelerate and expand the effort to demonstrate the feasibility of Raman based fiber optic sensors and add a new effort for developing a fiber optic based heavy metal sensor system based on Laser-induced breakdown spectroscopy.

### **Project Description:**

The fiber optic sensor group at NRaD (S. Lieberman, principal investigator) was responsible for the original development of the fiber optic based POL sensor that is currently used on the SCAPS system. Lieberman's sensor group has also published the most detailed studies to date on the effect of variability of the soil matrix on the response of fiber optic based chemical sensors. In addition, the NRaD sensor group is also breaking new ground on the use of artificial neural networks for pattern recognition of spectral fingerprints. Seven publications and three patent applications have been produced from this program over the last 3 years.

The objective of this effort is to demonstrate the feasibility of using two direct spectroscopic techniques that can be implemented using optical fibers: (1) Raman spectroscopy and (2) Laser Induced Breakdown Spectroscopy (LIBS) to extend the measurement capabilities of the

present SCAPS system.

Work under this proposal will be broken down into two major task areas: (1) Fiber optic based Raman Spectroscopy and, (2) Fiber optic based LIBS. In both cases the efforts will focus on establishing the feasibility (ie., limits of detection and specificity) of the respective spectroscopic method for a selected contaminant in real and simulated soil matrix. Work will be broken down under the two major task areas as follows:

1. Fiber optic based Raman spectroscopy. 1.1 Hardware Development: A fiber optic based Raman spectrometer will be developed that incorporates several technological breakthroughs which address problems that have until very recently limited the utility of Raman spectroscopy as an analytical methodology. These improvements include:

1) use of holographic notch filters for improved rejection of the Rayleigh scattered light, 2) use of cooled CCD array detector systems with very low background for improved signal to noise ratios, 3) use of a two fiber probe design that uses optical interference filters in conjunction with a matched lens system to insure optimal performance of the interference filters in order to eliminate unwanted Raman scattering from silica in the excitation and collection fibers, 4) use of new low wavelength high-power laser diode excitation sources. The prototype system will provide a capability for making measurements over fiber lengths of up to 100m in order to match the depth capability of the present SCAPS system. The fiber optic chemical sensor group at NCCOSC-NRaD currently already owns all major required pieces of instrumentation necessary for this effort.

1.2 Characterization of Raman returns for selected chemical compounds. The fiber optic based Raman sensor system developed in task 1.1 will then be used to demonstrate the feasibility of measuring selected chemical contaminants (ie., volatile aromatic hydrocarbons (eg., benzene, toluene, xylene) and various solvents) directly in soil samples. In addition, the sensor system will also be used to evaluate the measurement of biogenic gases such as methane and carbon dioxide that can be used to track the progress of bioremediation efforts.

1.3 Development of data analysis methods for real-time processing of Raman spectral data. Based on feasibility determinations in task 1.1, data analysis methods will be developed for processing information on contaminants with analytically useful Raman returns. It is proposed to use artificial neural networks in order to recognize and quantify the Raman signal from individual components in complex mixtures. The experimental plan is to evaluate artificial neural networks employing several different architectures (back propagation, learning vector quantizer (LVQ)) that use Raman spectra as the input and chemical species identity and concentration as the output. The neural networks will be trained using laboratory generated data sets measured using the fiber optic based Raman spectrometer developed in Task 1. Performance of different neural networks will then be evaluated and compared by testing the trained networks with spectra collected from test mixtures previously unseen by the network. The performance of the prototype neural networks for qualitative and quantitative discrimination of mixtures of different chemical constituents will be evaluated for the following specific tasks: 1) qualitative recognition of specific components in multicomponent mixtures after training the network to recognize all components in the mixture. 2) quantitative determination of individual components in multicomponent mixture after training the network with mixtures of the various components

at different concentrations. 3) qualitative and quantitative determination of selected components in mixtures that contain components not previously seen by the network.

2. Laser-induced Breakdown Spectroscopy (LIBS). LIBS is an analytical technique in which intense radiation from a laser is used to ablate material from a solid sample surface and form a hot plasma above the surface. The ablated particles in the plasma region are subsequently atomized and ionized. Analysis of the emission spectra from the hot plasma can then be used to provide simultaneous multi-element analysis of selected heavy metals. The feasibility of using LIBS for detection of Zn, Cr, Pb, Cu, Ni and Cd in soils at low ppm levels has already been demonstrated (Wisbrun et al., 1992). In fact these same workers have already reported a fiber optic based system that delivered the laser light to the sample over a 5 m length of optical fiber. The effort proposed here will focus demonstrating the feasibility of extending this methodology to longer lengths of optical fiber (50 to 100m) and developing a prototype sensor probe design that can be adapted to the cone penetrometer system. The prototype system will then be evaluated for determination of Zn, Cr, Pb, Cu and Cd in soils. The NRaD fiber optic sensor group already has possession of the high energy pulsed laser system necessary for this development and has the capability and demonstrated expertise in evaluating the performance of optical fibers for high energy pulsed laser sources (Theriault et al., 1992). In addition, S.Lieberman, has already established a professional working relationship with the group in Germany that established the initial feasibility of LIBS for environmental soil analysis and has a standing invitation for collaborative investigations.

The effort proposed here will directly support the DoD/DOE environmental objective for rapid, cost-effective methodology for site characterization and contaminant detection/delineation. Development of chemical sensors that can extend the capabilities of the cone penetrometer system for screening hazardous waste sites will: 1) save money by reducing the number of monitoring wells required to characterize a site, 2) reduce the time required to characterize a site because analytical data is provided in real time thereby reducing the number of sampling iterations necessary to define a contaminant plume, and 3) provide real-time information on the effectiveness of remediation efforts.

The following are tasks and activities related to the project for FY93-FY95. For FY93 (based on receipt of funds by end of 2nd quarter), complete fiber optic based Raman spectroscopy system for laboratory feasibility studies; characterize detection of selected chemical contaminants in soil matrices using the fiber optic based Raman spectrometer; and complete fiber optic based LIBS system for laboratory feasibility studies. For FY94, complete development of artificial neural network data analysis package for processing of Raman spectral data and complete laboratory feasibility studies for measurement of heavy metals in soils by LIBS. For FY95, conduct initial field evaluation of fiber optic based Raman penetrometer sensor for compounds for which feasibility has been established (eg., benzene, toluene, xylene, selected solvents, biogenic gases, etc) and conduct initial field evaluation of fiber optic-based LIBS penetrometer sensor for metals for which feasibility has been demonstrated in laboratory studies (eg., Zn, Cr, Pb, Cu and Cd)

For the Raman sensor, the most important issue is sensitivity of the technique for the selected contaminants in the soil matrix. Several aspects of the approach proposed here enhance the possibility for success. Most significant is the use of a cooled CCD detector system with extremely low background noise that permits longer integration times which results in

significant improvements in signal to noise levels. Also significant is the use of holographic notch filters for rejection of scattered laser excitation light. Other technical issues to be addressed include fluorescence from the sample matrix and variability in backscatter related to the changes in the sample matrix.

For the fiber optic based LIBS sensor for heavy metals, the most significant technical issues are transmission of high energy pulsed laser light over long (50 to 100 m) lengths of optical fiber, formation and stability of a plasma at the penetrometer probe/soil interface and matrix effects on the ablation/plasma formation.

#### **Expected Payoff:**

This technology has potential users both in the private and public sector. More than ten companies have already expressed interest in licensing the technology for the optical sensor for petroleum hydrocarbons. Similar interest is expected for sensors that would address other important classes of contaminants.

Cost estimates project savings of approximately 50% for site investigations. In addition, the optical cone penetrometer (SCAPS) will provide much more detailed vertical and horizontal data than can be obtained from conventional monitoring wells. The direct payoff of the real-time sensors is the ability to supply decision makers with detailed data on the location and type of subsurface chemical contamination at the site. This information will then permit more accurate delineation of the problem and the design of more appropriate and timely remediation responses. Intelligent real-time sensors for on-line monitoring of bioremediation systems could provide significant enhancements in efficiency by providing feedback for optimizing critical parameters.

#### **Milestones:**

For enhancements or past funded efforts, correlation of previously planned vs achieved objectives/milestones will be provided. Past efforts funded characterization of the fiber optic petroleum sensor in terms of variability of the sample matrix. This effort provided an understanding of the controlling variables for optical sensor response. This effort was documented in three separate published reports.

Projected accomplishments for the execution year (based on receipt of funds by end of 2nd quarter) are 1) Complete fiber optic based Raman spectroscopy system for laboratory feasibility studies; 2) Characterize detection of selected chemical contaminants (benzene, toluene, xylene, selected solvents) and biogenic gases in soil matrices using the fiber optic based Raman spectrometer; and 3) Complete fiber optic based LIBS system for laboratory feasibility studies.

#### **Transition Plan:**

Road map for transfer to next stage through implementation will be provided. Results of the effort proposed here will directly transition to the SCAPS (Site Characterization and Analysis Penetrometer System) that was developed under as part of a Tri-Service (Army, Navy, Air Force) effort and is currently being transitioned by all three services. NAVFACENGCOM is

directly supporting the transition of the Navy SCAPS system through DERA/SERDP Phase I funding by tasking NCCOSC to develop an advanced development model and specifications that will be provided to the NAVFAC field divisions for support of site investigations. The Navy specifications will then be available for Navy Clean Contractors to use for development of additional units.

Because of the Navy transition of the optical cone penetrometer system for petroleum, a line of communication has already been established between the user community (NAVFAC field divisions and the facilities) and the laboratory. Also, as part of the program to transition process the validation of this technology is being coordinated with the regulatory community.

**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
Navy/NCCOSC RDT&E	350K	400K
Army/WES	75K	100K

	<b>FY93</b>
DERA funds programmed for new start in Raman based sensors under Advanced Cone Penetrometer Sensors	100
POL sensor characterization	200
Investigation of the use of X-ray fluorescence for metal sensor	150

**Performers:**

The Navy/NCCOSC RDT&E Division would be the principal performer on this project. The effort would be coordinated with both the Army (USATHAMA/WES) and the Air Force. A collaborative effort with WES (P. Malone) is planned that would compare the neural network approach for sensor data analysis to methods based on multi-variate statistics. Dr. Lieberman has already established a professional working relationship with the group in Germany that established the initial feasibility of LIBS for environmental soil analysis and has a standing invitation for collaborative investigations.

Several companies have already expressed interest in commercializing sensor technology that would result from this effort. Discussions are in progress with several companies (eg., SAIC, Target, Inc and Hogentogler) about the possibility of CRDA's for commercialization of the technology to be developed in this effort.

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## **SERDP Thrust Area: Installation Restoration**

**Title:** Landfill Characterization System (LCS) Technologies Demonstration at the Kirtland Air Force RB11 Mixed Waste Landfill Site

### **Problem Statement:**

The goal of this effort is to demonstrate technologies that can provide additional characterization information on the KAFB RB11 landfill site. In the course of this demonstration, performance data will be collected to better assess the applicability of the technologies used to the unique problems in a mixed-waste site. This data will also provide both regulatory agencies and industry with a better indication of the commercial viability of these technologies.

The targeted departments for this activity are 542 CTW/EM at Kirtland Air Force Base and the Mixed Waste Landfill Integrated Demonstration (MWLID) located at Sandia National Laboratories funded by the Department of Energy, Office of Technology Development (OTD).

Currently, little is known about this site and any releases that may have occurred. At present, using existing OTD funding, interviews have been completed by MWLID staff with former employees to assist in ascertaining the materials buried at the site and the associated hazards that may exist to workers there. A "Cold Test" has been completed at an uncontaminated site immediately adjacent to the landfill to determine the geology and its relationship to the successful completion of this effort. This activity has never received SERDP funding.

### **Project Description:**

Following are some general statements of the technologies we would like to demonstrate at RB11. Each of these technologies has been demonstrated either in a hazardous waste landfill or uncontaminated site. They have not, however, been deployed in a mixed-waste environment. The management and cost of the previous demonstrations has been through the MWLID. The Integrated Demonstration program is under the DOE/ERWM/Office of Technology Development and has existed for several years and has successfully demonstrated many technologies. The MWLID has existed for approximately 1 1/2 years and has successfully fielded all technologies they have funded. An example of this is the completion of the "Cold Test" in the vicinity of RB11 already.

This activity is to include the placement of a "cold test" hole in an uncontaminated area in the immediate vicinity of RB11 to provide proof of capabilities. Success in the cold test may require modification of existing equipment for the site specific geological characteristics. If this occurs, the MWLID will provide the technical support necessary for those modifications. After a successful demonstration in the "cold test", we will drill two (2) directional holes in a "cross-trench" direction beneath RB11. The drilling activity will be conducted by Charles Machine Works (Ditch Witch®) using a prototype, developmental piece of equipment. It should also be noted that this technology does not produce secondary cuttings that may be mixed-waste.

Once the holes have been successfully completed, a flexible membrane liner, SEAMIST®, will

be emplaced for collection of pore vapors and for the deployment of downhole sensors. This technology was developed by SEA, Inc. using DOE funding and is in the process of being successfully transferred to the D&D activities of DOE. It's performance has not yet been demonstrated in a mixed-waste environment and several of the sensors have not yet been deployed in a directional borehole using the liner.

After membrane emplacement, downhole sensors, yet to be selected, will be deployed for logging the holes. In addition, borehole-to-surface technologies will be utilized to define trench boundaries, depths, and to confirm the number of trenches. Field screening techniques will be utilized to determine contamination.

Analytical results will be input into a sampling location analysis software called Plume®. This software, in conjunction with Site Planner® GIS software, will provide direction for additional drilling and sample collection as well as an excellent visual representation of the analytical results. Results from the cone penetrometer survey done by the USGS will also be incorporated into the system to provide to the Air Force as complete a picture of the site as possible.

#### **Expected Payoff:**

The successful fielding of these technologies should demonstrate a mechanism whereby assessments of mixed-waste landfills can be accomplished with reduced risk to personnel, minimal secondary waste streams, and at less cost to the site owner.

#### **Milestones:**

Initial background investigations, including interviews, and a "Cold Test" for proof of operation for the directional drilling technology. This work has already been accomplished using OTD funding. Identification of appropriate sensors to meet the problems identified during the interview process will occur during January 1993.

Winter of 1992-93 will be used to generate all Quality, Environmental, Safety, and Health documentation required to safely complete this demonstration. Coordination with Principal Investigators with individual technologies who will take part in this demonstration will also occur during this time.

The actual field demonstration of the technologies identified above will occur during the late spring and early summer of 1993. Associated with this are the logistics required to sustain an activity of this sort.

Input into the Site Planner software of efforts from this demonstration as well as ongoing USGS efforts and final report generation will be completed and delivered by the end of December in 1993.

#### **Transition Plan:**

The technologies demonstrated in the RB-11 project will be folded into the existing technology integration program for the Environmental Restoration Technology Department at

Sandia. The goal of technology integration is to facilitate the deployment of demonstrated technologies for use by DOE EM 30/40 and nationwide. This will be done through assessments of (1) regulatory feasibility, (2) industry endorsement, and (3) public acceptance. A regulatory analysis will be performed on the technologies demonstrated in the field. The technologies will then be reviewed by local state and regional federal regulators. During this review the regulators are briefed on the technologies, invited to view the technology demonstrations in the field, and asked for feedback on issues and concerns for widespread use. This regulatory review feeds into the commercialization plans for the transfer of the technologies. Workshops with potential federal and industry users of the technologies will then be held, at which the technologies are described, performance data is summarized, and there is direct exchange of information between users and developers. The final aspect of technology integration addresses the public acceptance of the technologies. The forums provided by the ongoing public participation activities for Sandia National Laboratories, Kirtland Air Force Base, and the MWLID will be utilized to gauge public acceptance of the technologies.

Established internal and external networks will be utilized for all three stages of integrating technology demonstration and evaluation with concerns of regulators, industry, and the public. Currently, the MWLID internal network includes the following organizations within Sandia: Community Outreach, Legal, Technology Transfer, Environmental Restoration, External Interfaces for ES&H, Education Programs, Environmentally Conscious Manufacturing, and Strategic Planning. These interfaces have brought about significant partnership opportunities. Within DOE/OTD, we have developed coordinated activities with other integrated demonstrations and DOE's technology transfer programs such as the Center for Applied Development of Environmental Technologies (CADET).

Industry partners in the MWLID and RB-11 projects will be supported by our technology integration program in the development of commercialization plans. Performance data from the field demonstrations will be combined with the feedback from regulators, potential users, and the public. This, supplemented by cost/benefit software analysis packages made available to the Technology Developers will comprise the plans.

**Funding: (\$K)**

FY93	FY94
620	90

The required funding for this activity is \$1,810K. Current OTD funds, utilized for demonstrations through the MWLID, are \$1,100K. Industry work, not included in the above estimate, being performed at their expense is estimated at \$450K. It should be noted that based on a successful demonstration this year, additional funding requests for remediation demonstrations in the out years may be made.

**Performers:**

The two federal agencies involved in this activity are the Department of Defense at Kirtland Air Force Base (542 CTW/EM) and the Department of Energy through the Mixed Waste Landfill Integrated Demonstration located at Sandia National Laboratories on Kirtland Air



Force Base.

Industries involved are Charles Machine Works (Ditch Witch®), Science and Engineering Associates, Inc. (SEA), Stolar, Inc., and ConSolve, Inc. The MWLID has existing funded activities through these partners and has secured their commitment.

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**SERDP Thrust Area:** Installation Restoration

**Title:** Feasibility Study for an Environmental Technical Support Center (ETSC)

**Problem Statement:**

The ETSC is being established for networking existing and emerging data systems to meet the following goals:

Support the Strategic Environmental Research and Development Program (SERDP) planning and programming process (Participating Agencies).

Identify environmental research and development information needs/deficiencies of users and structure ETSC services and products to meet these needs (Air Force);

Assist environmental planners, researchers, and decision makers by providing reviews, analyses, evaluations, and summaries of scientific/technical information on environmental quality issues in installation restoration, compliance, pollution prevention, energy, conservation, and remote sensing (global change) (Air Force).

Link available environmental data for federal, state, industry, academia, and NATO member/guest countries' users access (Air Force).

Develop tools to improve database integration to effectively target regulatory and compliance activities toward risk reduction (Army, Navy, DOE, EPA).

Effect mutually-beneficial data/technology sharing within the environmental activities of DoD, DOE, EPA, state, and local government agencies, and industry to meet environmental targets for cleanup, compliance, pollution prevention, conservation, energy, and remote sensing (global change) (Army).

Build ad-hoc teams of environmental, safety, and occupational health professionals to solve multidisciplinary problems by establishing data paths between organizations.

**Project Description:**

To accomplish these goals, the ETSC will require the services of a wide range of environmental experts plus numerous information management resources serving target areas. The ETSC will operate in a "distributed mode", utilizing existing resources (Integrated Access to Remote Environmental Army System (INAREAS) project results, etc.) at other locations and/or providing information referrals, collection, review, analyses, evaluation, and summaries to satisfy user requirements.

**Expected Payoff:**

The ETSC will facilitate SERDP planning and programming by providing users access to vital environmental information and expertise for improved project formulation, validation, evaluation, and approval. Plans/proposals generated through ETSC will enhance the

construction of joint research programs and the construction of the Tri-Service Environmental Strategic Plan. The ETSC will improve environmental decision making by promoting the exchange and sharing of scientific and technical information among the user community. Information provided by the users will be entered into the DTIC/DROLS Technical Report (TR) and work Unit Information System (WUIS), plus other service systems and clearinghouses already in place (e.g., Army's Environmental Technical Information Service (ETIS); Army's Automated Environmental Management Information System (AAEMIS); DoD's Environmental Bulletin Board System (DEBBS); Navy's Environmental Quality Information System (EQUIS); and EPA's numerous databases).

#### **Milestones:**

1. Determine User Population and Database Needs FY 93
  - Who are the users? 3 months
  - What are the most critical information needs and deficiencies?
  - What systems should be accessible?
  - What information will be provided, in what format, and how fast?
2. Inventory and Review Existing Data Resources 2 months
  - Define data requirements from Milestone 1 which can not be met by existing databases.
  - Identify existing databases which will meet the data requirements for Milestone 1.
  - Determine requirements (including hardware and software costs) to access the identified databases.
  - Identify the data structures and protocol for the identified databases. 3 months
3. Develop a concept for an effective data/technology interchange network based on the requirements identified in Milestone 1 and the data resources identified in Milestone 2:
  - Establish requirements for the communication network and its access.
  - Establish protocols for the extraction of the data from existing databases.
  - Establish costs for procurement of ETSC hardware and development of software.
  - Establish requirements and costs for hardware and software to access ETSC.
  - Establish costs for operation and maintenance of ETSC including software maintenance, distribution, and upgrade, and staff requirements.

#### **Transition Plan:**

The Air Force is establishing the ETSC to support existing SERDP Thrust areas. The ETSC will leverage existing scientific/technical expertise within federal, state, and local government, industry, academia, and NATO member/guest countries. ETSC will arm scientists, researchers, planners, and other decision-makers with the information to make informed decisions to resolve critical issues/needs.

**Funding: (\$K)**

	<b>FY93</b>
1. Analyze Needs	170
2. Inventory Data Resources	100
3. Develop Concept for Networking	<u>50</u>
Total	320

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## **SERDP Thrust Area: Installation Restoration**

**Title:** ECOTOX Data Base - A computer-based ecotoxicity support system for the establishment of hazard-based action levels and ecocriteria

### **Problem Statement:**

The goal of this project is to develop a comprehensive computer-based system that provides chemical-specific toxicity values for aquatic life, terrestrial plants, and wildlife. It is intended that this database will support consistent ecologically-based regulatory activities within EPA, DoD and DOE that are needed to implement remedial action plans at contaminated Federal facilities.

In the development and implementation of remedial activities at contaminated sites, EPA, DoD, and DOE are confronted with the need to establish scientifically-defensible clean-up goals that provide compliance with environmentally-based regulations. The lack of a comprehensive and current database of ecotoxicological information has hampered efficient and cost-effective collection and evaluation of hazard effect levels that are needed for these activities. Release of the ECOTOX system will represent an integration and stabilization of AQUIRE, PHYTOTOX, and TERRETOX, which are three existing EPA/ORD databases that contain ecotoxicity information for aquatic life, terrestrial plants, and wildlife, respectively.

This proposed project is a new SERDP effort.

### **Project Description:**

The three databases that will comprise ECOTOX are currently managed by two EPA Environmental Research Laboratories. AQUIRE, managed by the Environmental Research Laboratory-Duluth for the past 15 years, is current through calendar year 1991 and contains 108,524 individual test results on the effects of chemicals to aquatic life abstracted from 7,510 reviewed publications. Efforts are in progress whereby pesticide registration data from the EPA Office of Pesticide Programs are being incorporated. Toxicity data from member Organization for Economic Cooperation and Development (OECD) countries (e.g., The Netherlands, Germany, France) as well as Russia are being incorporated also. AQUIRE is maintained in FORTRAN on a VAX platform and made available to over 800 users in Federal, State, local, OECD, European Community, United Nations and other governmental bodies through the EPA National Computing Center (NCC) in Research Triangle Park. PHYTOTOX and TERRETOX were created approximately 10 years ago through the Environmental Research Laboratory-Corvallis. Although PC-based, PHYTOTOX is patterned after AQUIRE; because of funding limitations no data has been entered for the past six years and accessibility is very limited. TERRETOX is the least developed database, with incomplete software and no sustained data entry.

In FY92 a successful pilot program within EPA/ORD was undertaken to develop a prototype system that would provide the software framework to support ECOTOX and to initiate a re-write of TERRETOX software. AQUIRE is currently incorporated in the ECOTOX framework.

The objectives of this project are: 1) establish and maintain support of literature reviews and data entry for the databases that comprise ECOTOX, 2) refine and implement ECOTOX software, and 3) release ECOTOX to EPA, DoD, DOE, and other governmental agencies in a user-friendly on-line computer environment.

Two major and coordinated activities will be undertaken in this project. The first effort is focused on literature review activities that must be maintained to insure that ECOTOX provides current and appropriately reviewed data. The second effort involves database design and software development. ECOTOX will be VAX-based and released through the EPA NCC network.

ECOTOX will provide the means to cost-effectively collect standardized and critically needed data for the development of ecocriteria and thresholds for natural resource use at Federal facilities. Through a coordinated effort between EPA/DoD/DOE and other Federal natural resource trustees (i.e., NOAA, U.S. Fish and Wildlife Service) this project will facilitate consistent and integrated approaches to remedial action efforts for chemically-contaminated sites.

This effort will parallel an existing SERDP project addressing an interagency IRIS platform for human health.

Because of the EPA pilot project in FY92, minimal technical difficulties are anticipated. Peer-reviews will be held on quality codes to be used for each database and workshops will be held with users to establish priorities for filling data gaps in TERRETOX and PHYTOTOX, which have resulted from no funding over the last 6 to 8 years.

#### **Expected Payoff:**

Users of ECOTOX are expected to expand from the approximately 800 current users of AQUIRE. Use by DoD and DOE will result in more coordinated efforts within these two departments. Development and release of ECOTOX will provide EPA, DoD, DOE, and other Federal and State agencies a comprehensive support system that will increase efficiency and consistency in establishing hazard action levels and ecocriteria.

#### **Milestones:**

This effort has not been proposed in the past. ECOTOX software development would resume by mid-FY93 with a beta version release of February 1994. Following a 4 month evaluation period, final software revisions would be made for a September 1994 Version 1.0 release. Literature reviews would be resumed in all three databases; peer reviews and strategy workshops would be held (see below).

Milestones, with associated funding, for life of project are detailed below:

Date	Milestone	SERDP Cost
3/93:	TERRETOX & PHYTOTOX SOPs for literature reviews completed, strategy set	30K
3/93:	Literature reviews initiated	1,050K
5/93:	QA/QC Peer Reviews held; quality codes finalized	45K
9/93:	TERRETOX software completed; ECOTOX/PHYTOTOX integration	175K
10/93:	AQUIRE 1992 literature released	
12/93:	TERRETOX incorporated into ECOTOX	100K
2/94:	TERRETOX and PHYTOTOX literature equivalent to one calendar year released	
2/94:	ECOTOX beta version released	200K
5/94:	ECOTOX refinement from beta version initiated	150K
9/94:	TERRETOX/PHYTOTOX literature equivalent to one calendar year and AQUIRE 1993 literature released	
9/94:	ECOTOX Version 1.0 released through NCC	
	Total FY93/94	1,750K

**Funding: (\$K)**

FY93  
1300

SERDP funds have not been used, or requested, in the past. In FY92, EPA provided 165K to undertake the pilot ECOTOX effort. In addition, 1.25 EPA FTEs per year would be devoted to the effort.

**Transition Plan:**

ECOTOX will be released in 1994; strategy meetings with users and the release of a beta version will provide feedback for refinements. In the nearterm, DoD/DOE users will be incorporated into the current AQUIRE network.

**Performers:**

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DoD/U.S. Army Corps of Engineers/Mandatory Center of Expertise for Hazardous Toxic and Radionuclide Waste (Sandra Cotter)

DoD/U.S. Army Toxic and Hazardous Materials Agency/Environmental Services Branch (Jim Arnold)

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\* Note: The SERDP Scientific Advisory Board provided specific guidance to this project. Their position statement on this effort may be found in a separate section within this document; see "Table of Contents."



## **SERDP Thrust Area: Installation Restoration**

### **Title: Consortium for Site Characterization Technology**

#### **Problem Statement:**

Congress and the public are demanding faster cleanup of the Nation's hazardous waste sites. Delays in cleaning up a site may occur during the site characterization phase, the actual cleanup phase, or both. This proposal aims to accelerate the site characterization process, which is the necessary first step in any cleanup, by: (1) fostering collaboration among Federal agencies with substantial site cleanup needs; (2) encouraging innovation in characterization technology; (3) facilitating acceptance of new technology by regulators; and (4) encouraging the use of innovative technology.

When Superfund was enacted in 1980, cleanups were expected to be straightforward and rapid. Considerable progress has been made; however, the complexity and wide site-to-site variability of contaminated sites have greatly increased both the cost and the length of time required to clean them up. Delays in cleaning up a site may occur during the site characterization phase, the actual cleanup phase, or both. EPA is moving aggressively to accelerate the cleanup process. An example is the recently announced Superfund Accelerated Cleanup Model.

A major barrier to faster site characterization is the absence of a rapid way to gain acceptance of innovative characterization technologies by regulators, the courts, and the user community.

Site cleanup typically involves five steps: site characterization, risk assessment, selection of the appropriate remedy, remediation (including concurrent monitoring) and post-remediation monitoring.

Through, accurate characterization is essential for assessing risks at a contaminated site and for indicating the most appropriate remedy. It focuses on the nature and extent of contaminants, the site's geophysical attributes, and the condition of the ecosystem at and near the site. Often it is technically challenging, tedious, costly and slow. The potential to accelerate the characterization phase through innovations in characterization technology is very attractive. Furthermore, many innovative technologies suitable for site characterization also will be useful in the cleanup process.

Collectively, DoD, DOE, and EPA spent more than \$10 million in fiscal year 1992 on innovative site characterization technologies. Moreover, each agency has established programs that identify, test, and evaluate site characterization and related technologies. But emphasis on site cleanup has limited the attention given to monitoring, measurement, and site characterization technologies that a necessary forerunner of effective site remediation.

As new remediation technologies are now emerging, it is critical to facilitate parallel improvements in monitoring, measurement, and site characterization technology.

This proposal project was initiated in fiscal year 1992. The initial activity has been to brief the Department of Energy and Defense and private sector technology users. In addition, a

concept paper has been prepared.

### **Project Description:**

We propose to address the foregoing concerns by forming a partnership among the Department of Defense (DoD), the Department of Energy (DOE), and the Environmental Protection Agency (EPA). This will allow three Federal agencies with common needs to collaborate on the identification, development, and evaluation of innovative monitoring, measurement, and site characterization technologies.

Creating a Consortium for Site Characterization Technology (CSCT) to identify, validate, and encourage the use of the most cost-effective characterization techniques available.

We believe the Consortium approach is the cost effective way to satisfy the common needs of both and federal agencies and industry. Initially the Consortium will leverage resources from the three Federal agencies to pursue their shared objectives. However, our goal is to attract substantial participation by non-Federal cooperators.

The consortium will coordinate the work of member's researchers, which will minimize the chance for costly duplication of effort while maximizing the resources available for RDDT&E (research, development, demonstration, testing and evaluation).

The Consortium also will be an important mechanism for interaction between government and industry. This will help ensure that effective public private partnerships [for example, Cooperative Research and Development Agreements (CRADAs)] are formed as contemplated by the Federal Technology Transfer Act (fttA) and Executive Order 12591. Such interaction will stimulate both innovation and commercialization. Moreover, the Consortium's activities will likely improve the competitiveness of domestically developed technologies in international markets.

The CSCT will be a true consortium, and will draw financial and human resources from each member. EPA would administer and manage it. Related on-going EPA RDDT&E activities (for example, the Monitoring and Measurement Technologies Program) will contribute substantially to a strong technical foundation for the Consortium.

One of the Consortium's most important services will be facilitating the process by which innovative technology is accepted for use. It will coordinate the evaluation of new technology by all interested parties, including EPA Regional and Program Office officials. One of its most important products will be interagency recognition and acceptance of a method, roughly analogous to the familiar Underwriters Laboratory seal of approval. This will greatly facilitate acceptance of innovative characterization technologies by regulators and prospective users.

The Consortium will perform several related function, including, but not limited to:

Identifying and investigation promising new techniques for monitoring, measurement, and site characterization; Conducting laboratory and field demonstrations; Serving as a clearinghouse for monitoring, measurement, and site characterization information; Providing

technical assistance and support to DoD and DOE in their technology demonstration efforts; Providing a central source of information for and communication among industry and government technology developers and users.

Federal agencies have committed substantial resources to remediation activities, including development of new technology. This signals their high expectations that innovative technologies will reduce the duration and cost of site cleanups. Effective leveraging of resources among participating agencies through the Consortium should lead to realization of these expectations.

Initially the Consortium will include EPA, DoD, and DOE, but our goal is to attract substantial participation from the non-Federal sector. The Consortium will leverage resources and coordinate the work of members' researchers to minimize duplication of effort while maximizing the resources available for RDDT&E (research, development, demonstration, testing and evaluation).

During fiscal year 1993 a number of activities will be occurring. These include the preparation of an implementation plan, holding a number of Consortium Summit meetings within EPA, with DoD, DOE and EPA, and meetings to include the technology developer and user communities. An implementation strategy will also have to be prepared to identify the mechanism for accomplishing the functions of the Consortium. In fiscal year 1994 we expect the Consortium to begin assisting technology developers and users. The Consortium will ramp-up through fiscal years 1994 and 1995.

There are technical, regulatory, and policy issues that must be addressed and resolved early in the process of building the implementation plan (FY93). For the Consortium to satisfy its goals, EPA, as an Agency, must recognize and accept the methods for technology demonstration. The developer and user communities must have the confidence that the results of technology demonstrations are recognized by EPA.

#### **Expected Payoff:**

The Consortium will be an important mechanism for interaction between government and industry. It will help ensure that effective public-private partnerships are formed as intended by the Federal Technology Transfer Act (FTTA) and executive Order 12591. The resulting interaction will stimulate both innovation and commercialization. In addition, the Consortium's activities will likely improve the competitiveness of domestically developed technologies in international markets.

#### **Milestones:**

Consortium Summit meeting reports; Consortium Implementation Plan; and Agency and industry briefings.

#### **Transition Plan:**

See previous discussions under the Project Description section.

**Funding: (\$K)**

**FY93**

500

**Performers:**

Effective implementation of the Consortium will rely on the expertise and resources within DOE, DoD, EPA and the private industry user community. As mentioned previously, the Consortium will draw financial and human resources from each member. The Office of Technology Development (EM-50) in the DOE and the Office of the Assistant Secretary for the Environment (OAS(E)) in DoD have been briefed and have expressed an interest in supporting the Consortium approach.

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## **SERDP Thrust Area: Installation Restoration**

**Title:** Simulation of the Impacts of Subsurface Heterogeneities on Remediation Effectiveness

### **Problem Statement:**

The goal of this research is the improvement of contaminated groundwater resource cleanups on DoD/DOE installations through development of simulation models that predict the impacts of subsurface heterogeneities on remedial effectiveness.

All natural soils are heterogeneous. These heterogeneities significantly affect the transport and fate of contaminants in the subsurface on many scales, thereby exerting a primary controlling influence on contaminated groundwater remediation effectiveness. The ability to model, either numerically or physically, the impacts of heterogeneities on the efficacy of a given remedial alternative prior to implementation is inadequate due to the following:

(a) comprehensive, efficient, and tractable computational methods for conceptualizing heterogeneous subsurface conditions and processes based on the relatively sparse data taken at most field sites are unavailable. These conceptualizations, which represent one's basic understanding of subsurface geology, chemistry, biology, and hydrology, are the primary building blocks upon which all site cleanups are based. In the absence of these methods, the uncertainty associated with various conceptualizations cannot be quantified, leading one to potentially erroneous remediation decisions.

(b) the impacts of heterogeneities on several key natural processes affecting subsurface contaminant fate and transport, such as sorption or biodegradation, are unknown or lack systematic formulation. Parameters controlling these processes, which have been derived from bench-scale physical experimentation, are known to provide poor predictions of field-scale response. This is believed due to the effects of differing physical scales for the bench and field associated with the presence of heterogeneities. Thus, a primary set of input parameters required for fate, transport, and remediation modeling is known to be compromised, in a yet unquantified manner, due to the effects of heterogeneities.

(c) the relationships between media heterogeneity and several key anthropogenically-induced processes associated with promising in situ remediation technologies (such as the application of electrokinetics and the formation of biofouled zones due to additive incorporation) have not been adequately described for simulation.

(d) traditional-scale numerical models (i.e., Darcian-scale models, as all current models of general use are) do not capture the important flow and transport phenomena observed in heterogeneous media. These inadequacies are due to the failure of Darcian-scale models to properly account for influences of heterogeneities at smaller scales on flow and transport. The potential results of this inadequacy is the prediction of erroneous flow and contaminant transport patterns for natural soils.

## **Project Description:**

The objective of this research is the development of predictive numerical modeling technology that accurately and efficiently simulate the effects of subsurface heterogeneities on contaminated groundwater flow, transport, and remediation.

The proposed research project will be conducted in five highly inter-dependent major task areas: scaling criteria development, subsurface conceptualization, natural process investigation, remediation-induced process investigation, and numerical model development. The tasks proposed are themselves inter-disciplinary, generally requiring expertise from each of the three partnering agencies. Advantage will be taken of the unique facilities of the partners. For example, the intermediate-scale experiment proposed herein will be conducted by EPA in its facilities at the R.S. Kerr Environmental Research Laboratory (RSKERL), Ada, OK. Further, most of the visualization aspects of the program will leverage the Scientific Visualization Center and CRAY-YMP at DoD's USAE Waterways Experiment Station (WES). Computational skills at each of the partnering agencies will be leveraged. Additionally, the plethora of field sites available to DoD and DOE will be leveraged within the field experimentation component of the proposed research project. Previously well-characterized sites with contaminants of interest to DoD/DOE, such as the Air Force's MADE II site at Columbus AFB or the TCE site at DOE's Lawrence Livermore National Laboratory (LLNL, the major DOE partner in this proposal) will be utilized as appropriate.

The production-level products from the proposed research project will be incorporated into the DoD Groundwater Modeling System for dissemination to partners and throughout DoD.

The proposed project encompasses a major component of the unfunded portion of DoD's planned research under the Tri-Service Environmental Quality Strategic Plan, Pillar 1: Cleanup, Requirement Thrust 1.F: Groundwater modeling systems. The effort also contributes to the general requirements of DOE's Subsurface Science Program. The proposed research project both leverages and compliments DoD's ongoing work under the aforementioned Groundwater Modeling Systems thrust. The proposed effort also leverages ongoing work within DOE's Subsurface Science Program, ongoing remediation work at EPA's RSKERL, site characterization and remediation efforts within DoD (at WES) under the Installation Restoration Program, and DOE cleanup demonstrations at the Savannah River Plant.

The primary tasks within each of the five major task areas of the proposed research project are presented below. Inter-dependencies between the tasks are also provided as currently envisioned. Work within the task areas will run in a concurrent fashion, but will be phased where necessary to account for these inter-task dependencies.

I. Scaling Criteria Development. The term "scaling" herein is used to represent methods used for transferring information across temporal and/or length scales without the loss of details that are important to describing the process at hand.

II. Subsurface Conceptualization. Methods to quantify the geologic variabilities and uncertainties in parameters such as hydraulic conductivity will be developed. Geostatistical methods such as kriging, co-kriging and other statistical techniques will be used to quantify

the geologic uncertainty. The model of geologic uncertainty will then be coupled with geological facies models that are based on environmental deposition analyses to provide a comprehensive three-dimensional conceptual model of the subsurface. The ability to conceptualize or correlate other site characteristics, such as chemical composition or biological communities, will be added as appropriate. Three-dimensional, state-of-the-art visualization capabilities will be coupled with the geologic model to complete the conceptualization package. The conceptualization products will then be coupled with deterministic flow and transport models to provide an uncertainty-based modeling approach to groundwater contaminant fate and transport simulation.

III. Natural Process Investigations. Coordinated laboratory and intermediate scale investigations will be carried out to support scale-up of physical/chemical formulations for field-scale modeling of remedial alternatives under the Scaling Development task area. Processes affected by heterogeneity that will be investigated include the influence of soil chemical heterogeneities, competitive sorption, intra-particle pore phenomena, and facilitated transport. Processes will be investigated at both the bench and intermediate scale using EPA artificial aquifers to provide the information needed for scale-up of processes level descriptions.

IV. Remediation-induced Process Investigation. This thrust area will focus on processes which are induced during remediation of heterogeneous sites contaminated with organics and/or heavy metals. These processes are anthropogenic by nature in that they are a result of the deliberate injection of remediation additives into the subsurface. Examples of such additives include biotreatment nutrients (i.e. electron acceptors, nitrogen, and phosphates), surfactants, cultured bacteria, and extractants (chelating agents and acids). Investigation of the transport of remediation additives and changes in subsurface properties during the remediation process will be investigated with batch and column studies using soils with varying physiochemical properties. The soils and respective properties selected will be based on the target additive under investigation. This work effort will involve determination of retardation factors and utilization rates of the additives within the soil.

V. Numerical Model Development. This task area will act as the integrator for products developed in the other tasks. This task area will provide numerical modeling applications as a support for interpretation of physical experimentation at various scales. Models will be applied/developed in this task area in the following manner: (a) pore-scale models of flow and transport will be used as needed to provide a numerical laboratory for evaluating and modifying scaling theories developed in the Scaling Criteria task area; (b) highly-resolved continuum models similarly will be used to thoroughly test the utility and accuracy of proposed scaling methods; (c) practical, more coarsely-resolved engineering models will be used to simulate the laboratory and field investigations conducted in other task areas herein as a means of experiment interpretation and as a method for validation of process formulation development; and, (d) in concert with the Subsurface Conceptualization task area, geologic deposition modeling capabilities will be applied. Codification of process algorithms (from each of the process task areas), scaling methodologies, and conceptual modeling capabilities will be conducted in this task area. Finally, efforts within this task area will incorporate the improved process, conceptualization, and scaling formulations into the improved numerical models that will be coupled with the DoD Groundwater Modeling System (GMS).

## Expected Payoff:

It is envisioned that DoD, DOE, EPA, and their contractors will be prime users of the developed technology. Certain offices of the USGS, the USDA, and the Nuclear Regulatory Commission could also use the modeling developments and the guidance disseminated. Large environmental cleanup consulting firms, who are generally contractors of one of the three partnering agencies in this research project already, would probably request the models, reports, and technical expertise of the agencies as appropriate. Universities having extensive programs in hydrogeology, subsurface remediation, and groundwater modeling might also use the research products.

## Milestones:

	Task Area	Date
• Conduct rigorous review of propriety of using various geostatistical techniques such as kriging, co-kriging, etc.	II	FY93
• Couple geostatistics and facies modeling with environment of deposition analyses to form rudimentary geologic model	II/V	FY93
• Couple visualization to rudimentary geologic model	II	FY93
• Review available scaling techniques for critical scale-dependent processes and initiate scaling criteria development	I	FY93
• Initiate bench-scale studies on how remediation-based processes impact soil fabric and how those fabrics impact proper transport and utilization of additives	IV	FY93
• Select, collect, and characterize soils, aquifer materials, and chemicals of interest, and develop analytical protocols	III	FY93
• Select facilitated transport mechanisms for study	III	FY93
• Set up intermediate scale experiments for selected processes	III	FY93
• Initiate improvement of pore-scale models for use in scaling analyses and interpretation of physical experimentation	V	FY93
• Initiate improvement/development of geologic models based on environments of deposition	II/V	FY93
• Conduct pore-scale and highly-resolved continuum simulations as part of scaling analyses, and in support of remediation and natural process investigations at multiple scales	V	FY94
• Enhance/develop (as appropriate) less-resolved models for engineering application that are based on pore-to-macroscopic scaling criteria developed in concert with the scaling task area	V	FY94
• Initiate batch testing of chemical interphase transfer phenomena	III	FY94
• Initiate competitive sorption and intra-particle pore phenomena experiments at the bench scale	III	FY94
• Initiate intermediate scale experiments	III	FY94
• Document advancements in process descriptors for heterogeneous systems	III	FY94
• Initiate data base development and experiments for testing scaling procedures for heterogeneous conditions	I/III	FY94
• Complete development of initial scaling procedures	I	FY94
• Verify initial geologic model	II	FY94
• Initiate coupling of uncertainty analysis methods to geologic modeling package. Couple the package to the DoD Groundwater Modeling System	II/V	FY94
• Update DoD Groundwater Modeling System flow, transport, and	V	FY94



remediation models based on interim findings from this research project		
• Design and initiate intermediate scale studies to verify remediation-induced process concepts derived from the bench studies and further refine modeling techniques	IV	FY94
• Design a field-scale evaluation of the process formulations developed at smaller scales for remediation-induced phenomena	IV	FY95
• Extend uncertainty analysis features of the geologic model to aid user in field sampling design and Monte Carlo simulation	II	FY95
• Initiate field-scale evaluation of criteria at national test sites, if appropriate	I/III	FY95
• Conclude and document intermediate scale experiments	III	FY95
• Evaluate single-solute and ion exchange isotherms	III	FY95
• Document alternative model equations and formulations	V	FY95
Demonstrate improved predictive capabilities		
• Continue development and testing at lab and intermediate scales of engineering models; begin field-scale evaluation of modeling tools	V	FY95
• Complete work on final process descriptions	III/IV	FY96
• Analyze and evaluate data and integrate into process descriptions	III/IV	FY96
• Correlate process descriptors to grain size, soil organic carbon, CEC, etc.	III	FY96
• Complete field-scale remediation process evaluation	IV	FY96
• Complete short-term field demonstration of the geologic modeling package	II	FY96
• Document field application and testing of final scaling procedures	I	FY96
• Complete field-scale application of improved macroscale, engineering models with pore scale closure. Incorporate latest improvements in process formulations from companion task areas.	ALL	FY96

#### Transition Plan:

A roadmap for transfer to next stage through implementation will be provided. The roadmap for implementation of the products from this research follows the DoD Tri-Service Environmental Quality Strategic Plan Program, Pillar I: Cleanup, Requirement Thrust 1.F: Groundwater Modeling Systems. All of the computational products developed will be incorporated in the DoD Groundwater Modeling System, versions 1.0 and 1.5. Training and technical support in the use of these products for DoD personnel and designated contractors, as part of the DoD modeling systems, will be provided under the auspices of the proposed DoD Groundwater Modeling Technical Support Center. Partnering agencies would be provided the DoD modeling systems, complete with documentation, computer demonstrations, and software, as part of this research project. Technical support and training in the use of the system would also be provided to partnering agencies and their designated contractors on a generally reimbursable basis.

#### Funding: (\$K)

<b>FY93</b>	<b>FY94</b>
4310	6610

**Performers:**

The performers for this research project are: DoD (Army) - USAE Waterways Experiment Station, Vicksburg, MS; DoD (Air Force) - Armstrong Laboratory/EQ, Tyndall AFB, FL; DOE - Lawrence Livermore National Laboratory, Livermore, CA; and, EPA - R.S. Kerr Environmental Research Laboratory, Ada, OK.

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**SERDP Thrust Area: Installation Restoration**

**Title:** Development of Military IRIS System for the Hazard Identification and Risk Assessment/Characterization of Defense Related Pollutants

**Problem Statement:**

The goal of this research project is the development of a multi-level integrated risk information system for EPA/DOE and DoD. This project builds upon the current Phase I system for developing, sharing and transferring chemical specific health risk information, assessments and methods. This effort will be expanded to include research for the development of interactions data and methods for the risk assessment/characterization of defense/energy related chemical mixtures.

DoD/DOE activities involve industrial processes and large-scale operations that often result in soil, sediment and ground or surface water contamination. These pollutants include a wide variety of chemicals such as munitions, solvents, fuels and manufacturing byproducts. The defense community is currently charged with cleaning, correcting and maintaining these operations, 116 of which are superfund NPL sites. The EPA has developed systemic methods for identifying, characterizing and assessing the potential risk to human health resulting from exposure to these various contaminants. In addition, the EPA has also developed a high quality, timely scientific and technical information system for coordinating this risk information. Currently this system is used throughout the Agency (EPA) by all risk assessors and managers for the implementation of regulations and remediation of Super fund sites. This project, which was initiated under Phase I, will continue to build upon the current EPA systems and will be enhanced to include chemical mixtures, and site specific exposure data and risk characterization information for defense related operations. Identify whether this is a new project or enhancement to an existing funded effort: This is an enhancement of Project II-B6 under Phase I - Development of Military IRIS System to Augment Current IRIS.

**Project Description:**

The U.S. EPA's Integrated Risk Information System (IRIS) is one of the primary tools used by Agency scientist, programs offices, regional offices and ORD laboratory facilities for implementing regulatory actions, site remediation and identifying priority research and testing needs. In addition, this system and its supporting risk assessment methodologies are utilized nationally by state and local governments as well as internationally by WHO, PAHO and Health and Welfare in Canada in establishing clean-up targets and health impacts. Under Phase III, the acquisition and verification of chemical specific risk information and subsequent development of a military delivery system augmenting the existing EPA system IRIS to address the specific needs of DoD/DOE would be continued. In addition, a process is being developed to address generic as well as chemical specific risk assessment risk characterization issues and to improve chemical specific risk assessment methods.

Under Phase III, assessments and applied research for chemical specific risk assessment data, mechanisms of action and methodology will continue. These efforts, however, will be expanded to include interaction data and mixtures approaches and assessments.

Regular meetings (quarterly) will be held with representatives from Tri-Services, DOE and EPA Program offices as well as the Office of Research and Development.

An advisory group will be developed to select priority chemicals, site specific issues or generic issues to be addressed by Technical Workgroups. Site specific or chemical specific risk assessment approaches and/or validate methodologies or approaches. Consensus data and assessments will be provided for Agency verification and use on military IRIS. For mixtures, in particular, specific research issues for 3 specific mixture approaches will be identified initially (response or dose addition, interactions and Hazard Indexing). Data gaps and research needs for risk assessment methods/approaches for mixtures will be identified/discussed and conducted. Data and methods/approaches developed will be used to develop site specific remediation hazard/risk assessments for DOE/DoD sites or issues (i.e., RFD for diesel). These assessments can be applied to set clean-up standards for defense related sites or developed on Interagency RfC/RfD or cancer unit risk for IRIS. In addition, a mixture database will be provided using EPA MIXTOX database as a prototype.

The tasks identified for successful completion of this project include the development of Interagency Advisory Panel to identify mixture assessment issues, to develop draft document prioritizing research topics/approaches, and to evaluate current mixtures data and databases. Additional tasks include to develop database for mixtures building upon EPA MIXTOX database, to develop testing protocols (where appropriate) to provide data and validate approaches and lastly, the continuation of chemical specific work under Phase I.

#### **Expected Payoff:**

This project will improve methods for site specific remediation for EPA and DoD/DOE providing a more realistic approach for multimedia, multichemical exposures resulting in greater Interagency cooperation, reduction of remediation costs and potential litigation. Enhance EPA mixtures guidelines currently undergoing revision and to enhance mixture database. The potential users include DoD, DOE and EPA scientists, risk assessors and risk managers.

#### **Milestones:**

Development of Chemical specific Assessments/Verifications	Ongoing
- Continuation of Phase I	
Develop Mixtures Advisory Board	Sept. 1993
Conduct Mixture Expert Workshop	April 1994
Draft Research Need/Issues Document	June 1994
Update MIXTOX Database	Dec. 1995
Updating IRIS Database	Ongoing
Development of Database Management	Dec. 1995
System for Mixtures Data to Augment	
Current Military IRIS under Phase I	
Develop and Validate Mixtures Approaches	Sept. 1996

**Transition Plan:**

Co-equal partners in development of needs for research strategies and approaches. EPA will be lead agency for database management system IAG with DoD/DOE. This will be a cooperative agreement, EPA-ORD. See Milestones for breakdown of Transition Plan.

**Funding: (\$K)**

FY93	FY94
1000	500

**Performers:**

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## **SERDP Thrust Area: Installation Restoration**

**Title:** Toxicology and Human Health Risks

### **Problem Statement:**

The US EPA has established 5 part per billion Maximum Contaminant Levels (MCL) for trichloroethylene (TCE) and tetrachloroethylene (PCE) in drinking water based on "public policy driven" risk calculations and interpretations of scientific findings. TCE is the most common groundwater contaminant encountered at National Priority List (NPL) landfills on AF bases and PCE is frequently encountered. These chemicals are also common groundwater contaminants at non-AF NPL sites also. The risk based cost for clean-up of TCE (and PCE) is estimated to be in the multi-millions of dollars. Using FY92 SERDP monies (\$1 M), the Toxicology Division has begun a research program to address many of the health related issues to chronic low level exposure to TCE and PCE. The ultimate goal of this research proposal is to establish a joint venture between the Toxicology Division and the US EPA (and US EPA sponsored university researchers) to address several scientific issues related to the health risks that TCE and PCE pose. In addition, a nationally recognized research scientist in risk assessment from industry (Dow Chemical) would collaborate with us. The proposed research for FY93 monies would represent an enhancement to the FY92 SERDP new start.

To date, the Toxicology Division has presented to the US EPA PK(pharmacokinetic)-focus group human liver cancer risk calculations for TCE (using physiologically based pharmacokinetic modeling). The PK-focus group consists of US EPA individuals from most of their program offices and FDA invitees. This research focused on estimating species dosimetry (mice and humans) and served as a refinement in the US EPA approach to estimating the human cancer risks from exposure to TCE. The Toxicology Division plans on presenting a refined PCE risk assessment to the US EPA-PK focus group in CY93.

### **Project Description:**

A first principle for toxicology is that a linear relationship exists between the dose of the administered chemical and the biological response. Regulatory agencies rely upon this concept to establish chemical exposure guidelines for chemicals that are experimental and human carcinogens. To extrapolate cancer rates achieved from high doses of chemicals (eg., rodent cancer bioassays) to very infrequent cancer rates at low doses of chemicals (eg., environmental concentrations), the US EPA uses a linearized multistage model which is based on administered dose. The Toxicology Division has been a national leader in the use of physiologically based pharmacokinetic (PB-PK) models which "translates" administered dose to target tissue dose; accounting for nonlinearities in chemical behavior in the body, such as metabolism. The use of PB-PK models to predict target tissue concentration has advanced the state of predictive toxicology and risk assessment. This methodology is now used by the FDA, US EPA, some state agencies and industry. It is the Toxicology Division's intent to go beyond our PB-PK dosimetry studies and establish links between tissue dose and biological effect (pharmacodynamics). Pharmacodynamics aspects of research will include accounting for liver and kidney metabolism in rodents and humans and examining the cellular responses of these tissues to TCE/PCE and their metabolites. This research effort will use state-of-the-art techniques in molecular biology and mathematical modeling to derive scientifically based

estimates of the risks posed to humans exposed to PCE and TCE.

#### **Expected Payoff:**

This joint venture between the US EPA and the AF (with industry collaboration) will provide a critical mass of nationally recognized scientists to address the key scientific questions concerning the ability of TCE and PCE to cause cancer in humans. These research findings would provide a sound scientific footing for reevaluation of the standard setting processes for TCE and PCE.

#### **Milestones:**

The FY92 SERDP funds were used to establish a rodent/human liver slice capability. Metabolism studies were started in December, 1992. These studies are important because qualitative and quantitative studies of TCE metabolism in human livers have not been carried out. Recent rodent studies have shown that metabolism of TCE and PCE is required for these chemicals to exert their toxic effects. In conjunction with the in vitro metabolism studies, we are conducting binary mixture metabolism studies in rats (TCE and monochloroethylene (vinyl chloride)). In many cases, TCE is hydrolyzed to dichloroethylene and vinyl chloride in the environment. Vinyl chloride is a human carcinogen, thus TCE imposes an indirect risk via environmental degradation to vinyl chloride. We have ordered a mass spectrometer to be used for analyses of metabolites. An experimentally based TCE dosimetry risk assessment is in press and an experimentally based PCE dosimetry risk assessment is in preparation. These studies will feed into the follow on research aimed at describing the biological events that occur at a cellular level in a target organ in response (pharmacodynamics) to the target organ dose (pharmacokinetics).

#### **Transition Plan:**

Over the last 20 years, there have been many toxicologic investigations on PCE and TCE and PCE, including humans studies performed in the 1960's and 1970's. More recently, in the last 10 years, several investigators have attempted to better understand the mechanism by which these chemicals cause cancer in rodents. It is apparent that these compounds are biologically activated when the liver metabolizes the compounds to metabolites that react with biological tissue. Today, there are 3 major players that are trying to quantitatively link mechanistic information on bioactivation of TCE and PCE with human health risks: AL/OET, the US EPA, and Dow Chemical Company. Prior to this proposal, individuals from these organizations (see Principal Investigator list) have worked together on an informal basis to address different aspects of TCE/PCE toxicity and tumorigenicity. Now we propose to work as a team, which includes university professors conducting research via US EPA cooperative agreements. This team will be composed of top notch scientists that are currently working in mechanisms of action and risk assessment. No one to date, has attempted to develop a biologically based risk assessment model for TCE/PCE. This effort will provide the necessary research to characterize the health risks posed by chronic exposure of TCE and PCE in human populations.

**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
AL/OET	1000	1000
US EPA	500	500

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\* Note: The SERDP Scientific Advisory Board provided specific guidance to this project. Their position statement on this effort may be found in a separate section within this document; see "Table of Contents."



## **SERDP Thrust Area: Installation Restoration**

### **Title: Enhanced Anaerobic Degradation of Jet Fuels in Groundwater**

#### **Problem Statement:**

The Air Force has documented over 1500 fuel spill sites requiring some form of decontamination or monitoring. Pump and treat technology alone is economically impractical for renovating aquifers contaminated with large quantities of fuel; the reason for this is because the dynamics of immiscible flow result in prohibitively long time periods for complete removal of organic phase compounds. The slow release mechanisms of aromatic hydrocarbons, which are relatively water soluble, serve also as a slow release mechanism in sustained groundwater contamination. In situ enhanced biodegradation is often recommended as a cleanup method. However, HQ AFCEA and EPA researchers have documented many problems with current aerobic degradation methods, including high costs. To date, the in situ biodegradation of fuel has been limited to aerobic processes which require large amounts of oxygen be provided to the subsurface to stimulate biological activity. Homogeneous transfer of oxygen is seldom achieved and this process can be very expensive when oxygen sources such as hydrogen peroxide are used. A number of these deficiencies were documented in the recent field test at Eglin AFB. This project supports SAG SON 04-82 documenting the need to develop cost effective technologies to treat contaminated groundwater. Also IRP Site Investigation Reports throughout the Air Force.

The research will provide MAJCOM engineers and their consultants studies for remedial action plans. HQ USAF/CEV and HQ AFCEE are strong advocates. The goal of this research is field demonstration. This is an ongoing joint program with EPA.

#### **Project Description:**

The objective for this project is to confirm anaerobic degradation of JP-4 jet fuel in laboratory column experiments. From these experiments, new methods would be developed to enhance in situ anaerobic degradation through addition of nutrients.

Aquifer material will be collected from a JP-4 fuel contaminated site to be used in the bench scale studies. The US EPA RSKERL has developed a specialized coring device and anaerobic glovebox hood to maintain the integrity of contaminated core samples. The cores will be transported to the laboratory for bench scale testing of nutrient/nitrate enhancement of biodegradation of the JP-4 hydrocarbons. Upon successful completion of the laboratory studies, a pilot scale enhanced in situ bioremediation treatment system will be set up and operated at the contaminated field site. A recirculating groundwater enhancement system will be utilized. The degradation of the JP-4 hydrocarbons, specifically BTX, will be monitored over time, as well as nitrate levels and concentration of intermediates from microbial nitrate utilization.

Two tasks are planned as follows: 1) To conduct bench scale laboratory studies for the determination of natural and enhanced rates of anaerobic biodegradation of JP-4 jet fuel hydrocarbons, specifically benzene, toluene, and xylene (BTX); contaminated aquifer materials will be used for these tests; and 2) to apply the same bacteria stimulation techniques to a JP-4

jet fuel contaminated aquifer.

This project is in the Air Force Environmental Quality Research, Development and Acquisition Strategic Plan and the Tri-Service Environmental Strategic Plan under the DoD Pillar 1: Cleanup; Requirement Thrust; Treatment of Fuels in Groundwater.

Relationship to other similar on-going or past work: AFCESA has a joint program with US EPA RSKERL to perform bench scale nitrate enhancement studies.

**Expected Payoff:**

According to EPA studies, anaerobic degradation of jet fuel hydrocarbon components may proceed at faster rates than previously thought possible. If biodegradation can be improved without the addition of oxygen, future contaminated site remediations will be simpler and less expensive. Optimized nutrient addition data to stimulate anaerobic biological decontamination processes will be documented in a technical report.

**Milestones:**

Mar 93	Design of field treatment system/purchase hardware.
May 93	Installation of field treatment system.
May 94	Complete testing of treatment system.
Jul 94	Final sampling.
Sep 94	Final report/design, operating & cost information.

**Transition Plan:**

Near term products of this technology endeavor will be technical reports and professional publications to keep government R&D agencies and their contractors informed of our progress. Once the technology is validated, design and cost data will be distributed to the service agencies and their contractors. Also, technical data sheets will be submitted to the MAJCOM's. Following a successful demonstration, the operating data, cost information, and scale-up design criteria will be transferred to HQ AFCESA/RAA to plan and perform a user-funded full scale demonstration which will lead to site cleanup.

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>	<b>Total</b>
300	200	500

**Performer:**

This effort will be performed by the US EPA RSKERL. Funding will be provided though a MIPR.

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## **SERDP Thrust Area: Installation Restoration**

### **Title: In Situ Aerobic Biodegradation of Hydrocarbon Fuels**

#### **Problem Statement:**

SAC SON 82-04 documents the need for the development of technologies for remediating contaminated groundwater. The jet fuel contamination problem has been documented in IRP site investigation reports throughout the Air Force. In situ bioremediation of fuels and solvents requires adequate nutrient and oxygen addition to enhance natural biodegradation. Current methods of in situ biological treatment often fail to provide adequate oxygen to metabolize fuel contaminants in groundwater. Problems with the rapid decomposition of hydrogen peroxide, nutrient induced plugging, and poor oxygen distribution have all been documented in previous field studies.

Highly effective bioremediation techniques are being rapidly developed to destroy groundwater contamination under controlled reactor conditions. However, there are no developed engineering techniques to deliver nutrients to the subsurface, achieving continued bio-availability for effective in situ remediation. Conventional cleanup technologies involve pumping contaminated groundwater to the surface for treatment. However, the flushing process can take decades. In situ cleanup technologies take the treatment process to the source of contamination. Enhanced aerobic biodegradation is theoretically effective for treating organics. Biodegradation rates are limited by the availability of oxygen. Sparged air and hydrogen peroxide have been used to supply oxygen to subsurface water. Air sparging can only supply low concentrations of oxygen. Hydrogen peroxide is expensive. It also tends to degrade so rapidly in an aquifer that oxygen is lost from solution if hydrogen peroxide concentrations exceed 100 ppm. In addition, iron precipitation problems associated with these techniques have not been overcome, limiting our ability to disperse nutrients throughout the area subsurface contamination.

In situ bioremediation of fuels and solvents requires nutrient and oxygen addition to enhance natural biodegradation. The addition of these chemicals often results in geochemical reactions that plugs the aquifer, reducing treatment effectiveness. Nutrient and oxygen addition is often based on the results of laboratory batch tests which can not simulate true in situ conditions. This naive approach has led to inefficient and under designed full-scale systems which fail to meet clean-up objectives.

AFCEE and AF/CEV advocate developing cheaper and more effective cleanup technologies. The goal is field demonstration. Results of this research will be used by contractors performing cleanup of Air Force and Department of Defense contaminated sites.

#### **Project Description:**

The technical objective of this project is to validate the ability of aphyrons (air or oxygen microbubbles) to support biodegradation of subsurface contamination cheaper and more efficiently than conventional subsurface oxygen enrichment techniques.

A further goal is to develop a series of diagnostic tests for analyzing waste site soils and

groundwater to select proper nutrient mix and oxygen source for effective use and operation of in situ bioremediation treatment technologies.

The project will also demonstrate novel methods of introducing nutrients and oxygen into an aquifer contaminated with jet fuels. The project will utilize state-of-the-art monitoring techniques to provide real time measurement of biological activity and to control the injection of nutrients and oxygen to match actual microbe demand.

Aphron generation equipment has been developed and is being refined in a current 6.2 effort. Pilot, laboratory scale tests have been performed examining various injection strategies. Optimum injection hardware will be designed and installed at the field site, most likely in a trench system to create an aphron zone through which the groundwater will pass. Monitoring wells installed upstream and downstream will measure oxygen uptake and contaminant degradation. Study of varying operating parameters will take place over 18 months. A cost analysis will also be performed.

This approach will use laboratory testing to develop diagnostic tests and field studies to verify their effectiveness in predicting geochemical reactions. At this time, no other agency, including EPA, is funding this area of research or development. This research is being coordinated with the EPA's Robert S. Kerr Environmental Research Laboratory which is also studying in situ bioremediation.

This approach will use laboratory testing to develop improvements to nutrient formulations and new methods of providing oxygen in situ. Field studies will then be performed utilizing in situ monitoring systems to provide real-time measurement of CO<sub>2</sub> production by microbes, in situ oxygen levels, and contaminant.

There will be a literature review of all bench and pilot-scale studies that have been done in this area. Followed by the development of a nutrient and oxygen delivery system controlled by in situ monitors in the aquifer. There will be a pilot-test of the integrated system which can monitor and feed back information on subsurface environmental conditions so an in situ bioremediation technology can be run in the most effective manner.

A pilot, field-scale aphron generation and injection system will be designed and installed at an actual well-characterized contaminated site. Performance effectiveness, cost, and optimum operating parameters will be determined.

A task will be performed to identify at least four simple soil and groundwater characterization tests that can accurately describe the geochemistry of any site. Another task will be to systematically apply this battery of tests at several different Air Force sites where either bioremediation has been attempted or is being considered. The tests will provide engineers with a prediction of adverse geochemical reaction and nutrient mixtures to reduce these reactions.

This project is in the Air Force Environmental Quality Research, Development and Acquisition Strategic Plan and the Tri-Service Environmental Strategic Plan under the DoD Pillar: Cleanup; Requirement Thrust 1J: Treatment of Fuels in Groundwater and Thrust 1N: Treatment of Fuels in Soil.

**Expected Payoff:**

There will be several deliverables resulting from this work. The result will be a Principals of Practice manual on the design, installation and operation of an aerobic in situ remediation method for a fuel contaminated aquifer. These improvements to in situ biodegradation will provide Air Force and DoD engineers with a more reliable and less expensive alternative for removing fuels from groundwater.

Colloidal gas aphrons are a stable emulsion of air in water. Therefore, a higher mass loading of oxygen can be supplied to groundwater without being limited by the solubility of air in water. In addition, once aphrons are injected into the subsurface, they are caught up in the surrounding soil. Water passing through the "aphron zone" acquires dissolved oxygen from the microbubbles. This approach should be cheaper and more efficient than sparged air or hydrogen peroxide. Recent laboratory pilot-scale experiments have demonstrated much higher oxygen levels in flowing groundwater downstream from the aphrone zone than is achievable by air sparging or hydrogen peroxide. In addition, aphron oxygen remains in the soil matrix for extended periods of time, allowing continued oxygen transfer to the groundwater. No other technology provides this level of efficiency. This effort will validate the technology in a realistic field situation. The principal deliverable will be full-scale design criteria for a complete groundwater remediation system using in situ aphron injection. A technical report will detail a full technical and cost analysis of the technology in comparison to existing remediation techniques.

Diagnostic testing of soils and groundwater could ensure an optimized nutrient and oxygen addition and promote more efficient and more economical full-scale site remediations. The principal deliverable will be a guidance manual to assist site remediation engineers in designing and operating the most efficient in situ bioremediation systems.

**Milestones:**

Jan 93 - Literature Review

May 93 - Site Selection and Characterization

Jul 93 - Development of Nutrient and Oxygen Delivery System

Sep 93 - Installation of Delivery System in the Field

Mar 95 - Operation of System for 1.5 Years

May 95 - Final Sampling

Jul 95 - Final Report

**Transition Plan:**

Following successful demonstration, initial technical results and cost data will be distributed in the form of Tech Data Sheets to MAJCOM and base-level engineers and in the form of peer-reviewed publications to the R&D community. One or two follow on field efforts will be planned with AFCEE to further validate the technology in different and more challenging field conditions. These field demonstrations would take place at IRP sites with substantial user funding. Design packages will then be distributed to Air Force design agents. Widespread full-scale implementation will depend on commercial development with definition to full-scale design, operation, and maintenance factors by HQ AFCESA/RAA.

**Funding: (\$K)**

FY93	FY94
400	1200

**Performer:**

This will be a joint AF/EPA project with Capt. Vogel and USEPA Robert S. Kerr Environmental Research LAB performing the research.

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## **SERDP Thrust Area: Installation Restoration**

**Title:** Encapsulated or Immobilized Enzymes, Bacteria and Nutrients For Remediation of Fuel Spills

### **Problem Statement:**

This project is designed to develop technologies necessary to field a demonstration project at a fuel contaminated DoD site. This demonstration would utilize the technologies developed in the laboratory as an adaptation of encapsulation and controlled release technologies currently being developed at NRL. Such a demonstration if successful should lead to the transfer of this technology to business.

The target for this research would be current DoD installations with leaking fuel tanks, or spills which require remediation. Such sites may be contaminated with jet fuels, diesel fuels, lubrication oils, solvents, or other materials which require long term bioremediation.

Current remediation includes the use of pump and treat, soil venting, land farming or dig and haul technologies, pump and treat, soil venting, and land farming often use a process of air stripping to remove volatile components. This release of hydrocarbons into the atmosphere causes air pollution, or the capture of all vented gas and the adsorption of contaminants on activated charcoal filters. Such processes are expensive if air pollution is to be avoided. In addition, nutrients and oxygen carriers are found to be rapidly utilized by bacteria and fungi and are not persistent to aid in stimulation of remediation when simply injected into the contaminated site. Such state of the art approaches often require the use of large amounts of added nutrients and oxygen carriers which often cannot survive in the environment long enough to reach the in situ spill site.

### **Project Description:**

It is known that naturally occurring bacteria and fungi are able to degrade organic contaminants (fuels) which have leaked into the subsoil. The limiting factors have been determined to be the availability of oxygen or reductant compound, nutrients, surfactants and for areas of very high contamination the marginal ability of bacteria to survive the often toxic levels of contaminants. Protective encapsulation techniques to improve the survivability of bacteria or enzymes need to be developed for regions where fuel concentrations are too toxic for the native bacteria to survive. Bioreactors also must be developed to supplement the in situ effort - such reactors currently suffer from both low volume rates and poor efficiency. Microencapsulation and controlled release technologies for the encapsulation of bacteria, enzymes, nutrients and oxygen carriers hold promise as a means of remediation of both trapped petroleum and heavy metals.

Known competent bacteria and fungi and natural consortia from actual spill sites will be entrapped in a complex microcapsule system consisting of an alginate and nutrient agar core coated with either a phospholipid layer or chitosan depending on the application. Such a system is capable of being dried to a powder form for storage and shipment while maintaining viability of the microbial population entrapped. Nutrients and oxygen carriers are to be entrapped in liposomes which are also capable of being stabilized by a chitosan overlayer



and desiccated to form a dried powder for reconstituting at the contaminated site. Such a system would provide a controlled release of nutrients and oxygen carriers or reductant, and phospholipids would also provide a source of nitrogen and phosphorus for the microbial community and serve as a bio-surfactant for the contaminant which will increase bioavailability and enhance remediation rates. Further efforts would be needed to develop nourishment technologies for anaerobic bacteria as well as the aerobic population. The alginate technology would be directly applicable to the development of high volume bioreactors where the use of entrapped bacterial consortia could be maintained in optimum conditions for the treatment of either soil slurry or groundwater. By use of technologies for the encapsulation of PDMS fluids which have a very high oxygen carrying capacity a bioreactor could be designed which would permit regeneration of the oxygen source without direct air injection, and which could be maintained at a fairly high level of contaminant due to the protective nature of the encapsulation process.

The following are tasks associated with the project:

- 1) Microencapsulation of microbes in degradable carrier.
- 2) Microencapsulation of nutrients and oxygen carriers in liposomes and /or microcapsules.
- 3) Develop freeze drying techniques to provide for long term stability in storage and shipping, and to optimize rehydration techniques for both the microbial consortia and nutrient packages.
- 4) Develop biosurfactants for injection in situ and for bioreactor use.
- 5) Develop techniques to allow adaptation of microencapsulated materials in high flow bioreactors.
- 6) Characterize DoD spill site for soil type, contaminant profile and microbial consortia. Use samples obtained for laboratory validation of the microencapsulation on actual contaminant sample.

This project is directly applicable to a wide range of DoD environmental restoration projects where current sites are contaminated with fuels, solvents or other contaminants which have the potential to be remediated by biotransformations. Due to the very high cost of current technologies and their impact on the DoD O&M budget it is desirable to develop effective, low cost technologies to attack contaminated areas. Many DoE sites are also contaminated by a range of organic contaminants to which the technology is directly applicable. Including many common civilian EPA mandated remediation efforts such as leaking fuel or oil storage locations where high cost current technologies creates a formidable economic drain on businesses and individuals.

Current ongoing work has been conducted at NRL as well as many other laboratories in microencapsulation of bacteria and live cells, in addition many agricultural research projects have also been ongoing to control the release of fertilizers and pesticides. This projects has adapted those technologies in a unique approach which utilizes the basic science base to attack a Navy mandated environmental need. The adaptation of this technology may also prove to be an ideal method to deliver nutrients to microbial consortia at sites which utilize bioventing.

All materials used in this project are non-toxic, and are readily biodegradable in the sub-surface environment. All bacteria and fungi are non-pathogenic. The materials used for

microencapsulation are derived from plant and animal sources and are freely biodegradable. All technologies are adaptations of microencapsulation techniques developed for agricultural or medicine. While there are no guarantees that the technology is risk free, all care has been exercised to ensure that no environmental harm will result, and little risk has been posed to workers.

### **Expected Payoff:**

The expected payoff of this technology is in two areas. First is the development of generic techniques for the restoration of contaminated facilities for the DoD and DoE, as well as civilian contaminated sites. Low cost biotransformations of contaminants would sharply reduce the cost of remediation when contrasted with current technologies. The basic technology should be applicable to a wide range of contaminants such as a wide range of distillate fuels, solvents, chlorinated compounds, and explosive materials when biologically based remediation is desired. This approach addresses the need for long term remediation by microencapsulation and controlled release, and in addition will provide a means to remediate areas that are too heavily contaminated to permit current technologies to be employed. A benefit is the development of techniques that may permit less expensive application of bioreactor technologies due to increased efficiencies of controlled delivery. A further benefit to DoD would be a technology which would allow environmental compliance without an undue strain on operational funding. Such a long term approach would allow less frequent application of nutrients which would maintain higher rates of remediation while at the same time reducing on site labor and material costs. It would add to the capability of DoD and DOE as well as U.S. industry to meet environmental goals using natural processes, enhanced with non-toxic, non-polluting materials which pose no additional environmental threat. Such a process will speed the rate of natural remediation, and allow the remediation of environmental sites which are not treatable by current technologies. The process for bulk fermentation of microbial populations is today an accepted low cost technology which is employed in the medical and agricultural industry. Low cost technical grade materials such as agar, alginate, chitosan, and phospholipids may be produced without additional environmental risk from sources which are commonly considered waste products. Controlled release allows for efficient use of nutrients and oxygen carriers, reducing the waste of such materials now experienced because of uncontrolled delivery with current technologies. In addition the use of a dried powdered product permits low cost transportation and storage of the material for immediate application when and where needed.

### **Milestones:**

Task 1: Microencapsulation of microbes

Feasibility of microencapsulation for bacteria and fungi in a biodegradable carrier.

Demonstration of technique in laboratory.

Demonstration of Bacterial viability following microencapsulation.

Demonstration of pilot plant technique for entrapment of bacteria and fungi.

Demonstration of bacterial and fungal growth from microcapsules in soil samples.

Demonstration of entrapment of wild consortia.

Scale up to pilot plant quantities.

**Task 2: Microencapsulation of Nutrients and Oxygen Carriers**

Demonstration of method for stabilization of liposomes with chitosan.

Demonstration of entrapment of potassium nitrate as oxygen source.

Determination of leakage rate for potassium nitrate from liposome/chitin carrier.

Determination of efficacy in use of liposome carrier.

**Task 3: Develop Freeze Dry Techniques**

Demonstration of ability of microcapsules to survive freeze drying and reconstitution in water.

Demonstration of ability to preserve entrapped microbial community by freeze drying in microcapsules.

Demonstration of improved viability of encapsulated microbes following entrapment and freeze dry preservation in microstructures.

Develop methods for increased dispersability of freeze dried microstructures.

Develop methods to freeze dry and preserve nutrient filled liposomes.

Demonstrate use of materials to enhance remediation rates in field.

**Task 4: Develop Bio-surfactant systems**

Demonstrate role of phospholipids as bio-surfactants for in-situ remediation.

Milestone: Demonstrate ability to entrap and deliver bio-surfactants to contaminated soils.

**Task 5: Adapt technologies for high flow bioreactor use**

Demonstrate activity of immobilized bacteria in large macrocapsules.

Demonstrate ability to utilize microencapsulated PDMS technology in this system to deliver oxygen to reactor.

Demonstrate ability of reactor to tolerate higher levels of hydrocarbon contaminants.

**Task 6: Chemical and Biological Characterization of DoD spill site, and use of natural consortia of microbes and actual contaminated soils in a laboratory bioreactor to predict success of microencapsulated systems to enhance the background remediation rates.**

Characterization of Collected Samples.

Characterization of Background Bioremediation rates.

Demonstration of Enhanced remediation rates by microencapsulated systems.

**Transition Plan:**

Transition planned for FY96, industrial partner would be selected for current standing in the field of agricultural microbial biotechnology. Suggested partner for production would be either Abbot, Alltech, or Eli Lilly agricultural products. Environmental engineering firms already in the area of remediation such as Sciteck (St. Louis, Mo.) or Ecova, or Envirogen. Transition to be complete by end FY97. First step would be CRADA relationship beginning 96.

**Funding: (\$K)**

**FY93**

350

**FY94**

500

**Performers:**

Naval Research Laboratory Code 6900

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**SERDP Thrust Area:** Installation Restoration

**Title:** Biodegradation Technology for Hazardous Waste Treatment

**Problem Statement:**

The goal of this project is to examine specific aspects of several recently identified biological systems for applicability to the on-going development of biological treatment technologies for the degradation of typical Air Force IRP contaminants.

Through the Installation Restoration Program (IRP), over 1,500 JP-4 jet fuel and 900 solvent contamination sites have been identified. Problems remediating these sites have been documented in IRP site investigation reports from throughout the Air Force. Typically, contaminated groundwater is cleaned by one of two methods: aqueous phase carbon sorption or air stripping. Both methods are effective in removing the contaminants from groundwater; however they do have their limitations. Aqueous phase carbon sorption is often costly and is not a destructive technique. The contaminants are simply collected and concentrated on the carbon producing a potential hazardous waste solid (i.e. the activated carbon). Air stripping is an effective treatment alternative, but it transfers the contaminant from the water to the air. In some instances this contaminated air stream is also regulated and requires treatment. This project supports SAC SON 82-04 which documents the need for the development of technologies for remediating contaminated groundwater. This is a new start project in FY 93.

**Project Description:**

Previous efforts/accomplishments in this n this area within and outside the organization: Biological treatment technologies are being developed at AL/EQ to overcome the limitations of physical/chemical treatment technologies. Many of the solvents (i.e. perchloroethylene or PCE) found at Air Force IRP contamination sites can only be biodegraded under anaerobic conditions. Research has been conducted on the reductive dechlorination of compounds such as PCE by an anaerobic microbial consortium. Complete dechlorination of the PCE molecule to ethylene has been demonstrated.

The technical objective of this project is to examine specific aspects of recently identified biological systems for applicability to bioremediation technologies for the degradation of typical Air Force IRP contaminants.

This laboratory research will focus on the biological dechlorination process for PCE. More Specifically, we will look at: (1) investigating alternate electron donors to circumvent completion for the donor by methanogens in the consortium; (2) acclimation and induction of the mixed culture; (3) microbial studies to isolate and characterize the dechlorinating organism. This research will be performed utilizing the same microbial consortium as used for previous research by Gossett, et al.

This project is in the Air Force Environmental Quality Research, Development and Acquisition Strategic Plan and the Tri-Service Environmental Strategic Plan under the DoD Pillar 1: Cleanup; Requirement Thrust 1M; Treatment of Solvents in Soil.

The US EPA Robert S Kerr Environmental Research Laboratory is currently funding research into the anaerobic degradation of PCE.

The engineering studies will use batch experiments as well as the bench-scale bioreactor used previously by Armstrong Laboratory Environics Directorate researchers. These studies will answer the questions concerning the applicability of alternate electron donors and the acclimation/induction of the mixed culture. The microbial consortium is the same as was used for previously AL/EQ-funded research. The microbial studies to isolate and characterize the dechlorinating organism will be accomplished using traditional microbiological laboratory methods.

**Expected Payoff:**

This research will provide DoD/DOE engineers and their consultants data to prepare and conduct feasibility studies for remedial action plans to remove contaminating solvents. Complete development and optimization of biological treatment technologies for solvent contamination will offer a cost-effective destructive method of treating contamination groundwater. A more through understanding of how the biological system works will reduce potential operational problems when they are transitioned to the field for full-scale testing and thus increase the probability of success.

**Milestones:**

Investigate Alternate Electron Donors	Jun 93 - Mar 94
Acclimation/Induction of Culture	Aug 93 - May 94
Microbial Studies	Aug 93 - May 95
Final Report	May 95 - Jun 95

**Transition Plan:**

The products of this research are technical reports and professional publications typically for the R&D community and Technical Data Sheets for distribution to the operational field (MAJCOM's and bases). The information and data generated will be incorporated into our on-going 6.3 and 6.4 in research efforts.

**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>	<b>Total</b>
AL/EQ 6.2	228	240	668
SERDP	400		400

**Performers:**

It is anticipated that a Board Agency Announcement (BAA) contract will be awarded to university researchers to accomplish this work.

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## **SERDP Thrust Area: Installation Restoration**

**Title:** In Situ Treatment of JP-5 in Unsaturated Soils

### **Problem Statement:**

The goal is to provide the Navy and DoD with cost-effective, on-site, and in situ methods to remove and destroy low volatility fuels, such as JP-5, which is the Navy's major IR pollution problem. The Department of the Navy is the targeted department, but the results should aid other DoD, Federal, and private agencies. This project is an enhancement of bioventing technology developed in field pilot testing of JP-4 by the Air Force, JP-5 by the Navy (NAS Fallon), and from successful European designs. Present cost-effective technologies for fuel remediation, such as soil venting, are inadequate for in situ treatment of low volatility fuels. Adequate methods for determining biodegradation rates of low volatility hydrocarbons and specific information concerning their biodegradation pathways is also lacking.

### **Project Description:**

A field pilot study is ongoing at NAS Fallon, where a one acre system is treating part of a large JP-5 subsurface plume. The main emphasis of this proposed project is to scale-up existing bioventing technology, using information generated from NAS Fallon and published studies biotreating diesel fuel and Jet Fuel A. This scale-up will be accomplished through conducting a well monitored field demonstration study, which will involve bioventing an entire 4 acre JP-5 subsurface plume that surrounds Tank #1253 at MCAS Kaneohe Bay, Oahu, Hawaii. Research will be concentrated in approximately a 0.5 acre subplot that dissects the plume radius. Additional field and bench-scale research will also be conducted, which includes assessing use of a vacuum extraction well system to accentuate free fuel removal from the groundwater table; using biomarkers and refractory internal biochemical tracers to determine specific biodegradation rates; quantitating biochemical, physical and chemical removal pathways; and correlating specific enzymatic activity with biodegradation rates. Such information could help in developing rapid field methods to assess bioremediation success. This site is well characterized from three RI/FA studies (over 80 borings and wells) and has both permeable and low permeable areas that can be compared for bioventing efficiency. The only fuel present is JP-5. In conjunction with this bioventing study, an in situ biofilter may be tested as a cost-effective method to remove vented hydrocarbon vapors, if sufficient vapors are extracted. In situ biofilters are enclosed surface soils, usually in the uncontaminated zone above the NAPL plume, into which off-gas vapors are injected and then withdrawn under vacuum. Air Force and U.S. EPA involvement in this study has been requested.

### **Expected Payoff:**

The major payoff would be an estimated annual savings to the Navy of 10 million dollars. Since JP-5 is similar to commercial Jet Fuel A and comparable to diesel fuels and JP-8, other DoD, Federal, and private agencies will benefit financially from this field research study. The savings are based on previous information showing in situ bioventing to be at least one third the cost of current technologies for destroying low volatile fuels, including above-ground, on-heap soil pile bioremediation. Additionally, in situ treatments are generally the most



readily accepted by the public. The most cost effective method to treat off-gases from soil venting, bioventing, or groundwater air stripping has been shown to be the use of biofilters. In situ biofilters are the most cost-effective process for treating low levels of fuel vapors since natural matrices are used and maintenance is very low.

#### **Milestones:**

	FY
Design Field Demonstration Bioventing System Based on Field Pilot Study Findings	93
Complete Field Soil Gas and Respirometric Evaluations	93
Complete Construction and Initiate Bioventing, Field Demonstration System at MCAS Kaneohe Bay	93
Construct and Initiate Research in Field Subplot	94
Construct and Operate In Situ Biofilter System	94
Complete Field Demonstration Study at MCAS Kaneohe	96
Compile Tech Assessment/User Guide on Bioventing Low Volatility Fuels	96
Prepare Tech Transfer Package on Bioventing Design, Efficiency and Use	96

Projected Accomplishments for the execution year include 1) Design Field Demonstration bioventing system, design field and laboratory research studies; 2) Conduct soil gas and respirometric evaluations at MCAS Kaneohe Bay; 3) Construct field bioventing pilot system at NAS Fallon, evaluate existing vapor-phase bioreactors, and system on 4-acre subsurface plume at MCAS Kaneohe Bay; and 4) Initiate bioventing and free product recovery at MCAS Kaneohe Bay.

#### **Transition Plan:**

The in situ bioventing treatment technology will be transitioned to DoD and industry. The Technology Transfer Package will be available by the end of FY96, unless unforeseen field problems arise that impede project completion by mid-year FY96. Both the DoD and private industry are expected to experience significant cost-effective innovative technology.

#### **Funding: (\$K)**

FY93	FY94
950	900

#### **Performers:**

Performers will include Navy/NCEL; Air Force/Tyndall (Environics); and U.S. EPA/RREL (Tentative).

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\* Note: The SERDP Scientific Advisory Board provided specific guidance to this project. Their position statement on this effort may be found in a separate section within this document; see "Table of Contents."

## **SERDP Thrust Area: Installation Restoration**

### **Title: Fuel Hydrocarbon Remediation**

#### **Problem Statement:**

The Navy/DoD have several hundred sites with fuel contamination, and remediation projects are necessary to comply with regulatory requirements for these sites. Gasoline, Diesel and JP-5 are the most common contaminants. Many of these sites are located in coastal areas with shallow to moderately deep ground water aquifer. The goal of the Test Site program is to conduct field demonstrations of technologies that can remediate fuel contamination and transfer of these technologies for implementations to other sites. The target organizations for tech transfer will include Navy, DoD and other agencies that have fuel contamination. The technology demonstrations will be of value to the industrial sector as well.

#### **Project Description:**

The original proposal was presented to the SERDP Scientific Advisory Board (SAB) on April 21, and May 18, 1993. During subsequent discussions, the SERDP SAB suggested amending the proposal to incorporate the following: (a) use of Broad Agency Announcement (BAA) process to identify novel technologies for demonstration projects to remediate fuel contaminated sites, (b) establishing a peer review panel to select technologies, review demonstration plans and technical reports, and (c) to initiate Phase I of this project during FY 93 at the Naval Construction Battalion Center (NCBC) Port Hueneme, CA. This phase involves the demonstration of enhanced soil bioremediation and one other technology for ex-situ treatment of fuel contaminated soil. This technology will be selected by the peer review panel from those submitted via the BAA process and will be also setup at NCBC for side-by-side demonstration along with enhanced soil bioremediation.

The focus of the BAA process will be to identify those technologies that have evolved through the initial stages of development and can be readily scaled-up for field demonstrations. For the BAAs, the spectrum of technologies for field demonstrations will include: ex-situ treatment of contaminated soil, ex-situ technologies for ground water remediation, and integrated technologies for in-situ remediation of contaminated soil and ground water. The first BAA will be for on-site, ex-situ remediation of fuel contaminated soils. Announcements for other demonstrations will be developed as the program progresses. These announcements will be published in the Commerce Business Daily (CBD).

The peer review panel will be comprised of five individuals and two alternates. The alternates will act as panel members if for any reason the original members cannot participate in the technology review and selection process. The prospective members include: Dr. Martin Reinhardt - Stanford University, Dr. Lewis Semprini - Oregon State University, Mr. Anthony Tafure - EPA Risk Reduction Engineering Lab, Dr. Richard Watts - Washington State University, Dr. Lorne Everett - Geraghty & Miller, Inc; and Drs. John Ferguson and Paul Roberts - University of Washington, Dr. James Vanyo - University of California Santa Barbara.

#### Phase I: Ex-situ Treatment of Fuel Contaminated Soil.

The demonstration of technologies for on-site treatment of excavated soil will be conducted at the NCBC. At this location fuel leaks from underground storage tanks have caused soil and ground water contamination. Over the next 9-12 months, NCBC is planning to remove 50 USTs and is expected to generate about 17000 yd<sup>3</sup> of gasoline and diesel contaminated soil. At the NCBC, about 1000 yd<sup>3</sup> of gasoline and diesel contaminated soils were generated from previous tank removal and other activities. On-site treatment of these two batches is in progress. The NCBC has constructed an engineered soil staging area and a permit from the Regional Water Quality Control Board (RWQCB) is in place. For gasoline contaminated soil the permit limits include benzene at <0.3 mg/kg and Total Petroleum Hydrocarbons (TPH) at <100 mg/kg. For diesel contaminated soils, the TPH limit is <250 mg/kg. The Board established these requirements following a public hearing.

The technology demonstration for on-site treatment of excavated soils are planned at the current staging area and is not expected to adversely impact the on-going operations as the staging area is fairly large (about four acres). The limits specified in the existing permit will be applicable to technology demonstration during Phase I of the project. The Phase I involves demonstration of enhanced soil bioremediation and one other technology that will be selected through the BAA and peer review. The demonstration will be designed to obtain side-by-side performance data for the two technologies.

#### Phase II: Ex-situ Treatment of Fuel Contaminated Ground Water.

The proposed test site for demonstrating ground water treatment technologies is a NCBC site where gasoline leaks from a gas station contaminated the underlying ground water. The site has been characterized over the past several years and there are more than 30 monitoring wells at the site. Tests have also been conducted to determine aquifer properties. An interim corrective action required by the regulatory agencies is in place. This involves ground water pump & treat, and soil vapor extraction (using spray aeration-vacuum extracting system). The main objective of this interim action is plume control to avoid further spreading of the contaminated ground water.

This gasoline leak site is proposed for demonstration of ex-situ ground water treatment technologies that will be selected through the BAA process. The gasoline plume at this site is spread over more than five acres and due to the large size of this plume, technology demonstrations can be conducted at a portion of this plume without significantly impacting the on-going interim corrective action. As most of the site characterization work has been done, significant time and cost savings for actual demonstrations can be realized by using this site. However, additional site characterization may be needed prior to assessing any specific technology that may be selected.

The existing National Pollution Discharge Elimination System (NPDES) permit will have to be modified to accommodate any new technologies. This permit sets limits on contaminant concentrations (e.g., benzene at <1 ug/l) in treated ground water. The regulatory agency, RWQCB, is expected to allow technology demonstrations at this site. However, all technologies will have to meet the same limits that are specified in the current permit. The start of Phase II is proposed during year 2 of this project.

### Phase III: Integrated Technologies for In-situ Remediation of Soil and Ground Water.

The emphasis of these technologies is on in-situ techniques for both soil and ground water. The technology selections for Phase III will be also based on the BAA and the peer review process which will be initiated during year 2 of this project.

#### Expected Payoffs:

This program addresses the most common source of contamination at Navy sites, i.e, Fuel Hydrocarbons and hence the information developed from these projects will be applicable for cost effective remediation of a large number of Navy sites. In addition, the scope of the technologies selected for the field demonstrations cover both the soil and ground water contamination and therefore will have wide scale applications.

The hydrogeological characteristics of the NCBC location are similar to many coastal areas and thus the data collected from field demonstrations will be applicable for a large number of sites. The site has moderate to high permeability soils, shallow aquifer, and an aquitard that separates the shallow aquifer from deeper aquifers.

#### Milestones:

Task	FY93
1. BAA and Technology Screening for soil treatment	30
2. Peer review (travel costs for members)	15
3. Modification of existing permit	15
4. Field Demonstration Plan	135
5. Site Safety Plan	50
6. Characterization of excavated soil	150
7. Field Demo (soil bioremediation)	350
8. Project Administration	<u>150</u>
Total:	895

During the project year 2, demonstration of enhanced bioremediation and of one other technology (to be selected through the BAA and peer review process) for ex-situ treatment of soil, will be completed. The cost estimate for this second year effort will be developed upon selection of the second technology.

The outyear demonstrations will focus upon ex-situ ground water treatment and integrated technologies for in-situ remediation of soil and ground water. Outyear cost estimates will be submitted as the project progresses through the BAA process and specific technology selections.

#### Transition Plan:

The transition of demonstrated technologies to NAVFAC Engineering Field Divisions (EFDS) will be carried out jointly through the co-located Naval Energy and Environmental Activity that has dedicated technology transfer teams. Similar organizations from other services and

agencies will be afforded opportunity for access to data on technology transfer. The use of a BAA mechanism will greatly facilitate technology transfer.

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
895	990

**Performers:**

NCEL, NCBC Port Hueneme, NEESA, NAVFAC EFD, AFCESA, and other DoD agencies.

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**SERDP Thrust Area:** Installation Restoration

**Title:** A National Bioremediation Field Research and Demonstration Initiative, Wurtsmith Air Force Base, Oscoda, MI

**Problem Statement:**

The goal of this project is to establish a national bioremediation field research facility to conduct controlled field tests on in-situ remediation of contaminated soils, groundwater, and sediments.

The need for controlled field research and demonstration programs on bioremediation technologies has been documented in numerous studies and reports generated by internationally recognized remediation experts. Recommendations for establishment of a national bioremediation field facility have been made by several organizations, including the Bioremediation Action Committee, a joint federal government, industry and academic working group that is encouraging the development of bioremediation; the five EPA-sponsored regional Hazardous Substance Research Centers (HSRCs), and the Remediation Technology Development Forum, an industry lead task force focused on working with the federal government on improving the development of environmental clean-up technologies for hazardous waste sites.

This project is an enhancement to an existing EPA funded (FY 92 - \$275K, and FY 93 - \$500K) effort. Joint FY 93 funding of this project by the U.S. Air Force is expected. In FY92 and FY93 DOE has provided \$750K annually in support of the five HSRCs. A portion of these DOE resources is for bioremediation research at these centers.

**Project Description:**

Field studies and demonstrations of in-situ biotechnologies conducted to date have not provided the level of information required, largely because they have not been carried out under sufficiently well planned, controlled, and monitored conditions. A major problem in the development of bioremediation technology is the lack of field sites that are well-characterized with respect to contaminants, geohydrology, and geochemistry; such are urgently needed for understanding the natural events that are taking place and also for the transfer technology developed in the laboratory to field conditions. The type and level of information required for development of an appropriate protocol for biologically centered remediation design can be obtained only from well-planned and carefully controlled field experiments and demonstrations, including parallel evaluations of alternative approaches.

The technical objective is to conduct controlled tests of alternative bioremediation approaches and processes in the field and to provide information necessary to design and engineer effective systems. Proven bioremediation technologies need to be developed for direct application at DOE, DoD, and Superfund sites. Closer correlation of laboratory and field results is an associated objective for these needs.

The technical approach will be to establish the Wurtsmith Air Force Base (AFB) as a national test bed field research and demonstration facility for in-situ bioremediation technologies.

There are several reasons why Wurtsmith is an ideal site for the facility. The Base:

- presents an extensive and appropriate set of contaminants and remediation conditions involving a variety of absorbed dissolved and non-aqueous phase petroleum hydrocarbon mixtures, chlorinated solvents, heavy metals, PCBs, and PAHs;
- presents excellent geologic and hydrologic properties and is well characterized from 12 years of USGS involvement;
- has already had contaminant levels identified for most of 43 areas of contamination and several conventional pump and treat systems are in place;
- has three surface water areas (a lake, river, and wetland) connected with the aquifer that present excellent conditions for field research, including remediation of sediments;
- can benefit from the proposed research to accelerate the remediation at the site;
- will be controlled by a regulatory agency, the state of Michigan, and the Michigan department of Natural Resources, which supports the research proposal;
- is immediately available for use as a research and development site.

An important aspect of this approach is to use the Base's existing areas of contamination with well-defined hydrogeology, contaminant levels, plume boundaries and sampling locations to conduct controlled field experiments for *in-situ* bioremediation. Field studies will generally include treatability studies, scale up of laboratory experiments and demonstration scale evaluation of potential site remediation treatment trains.

DoD and DOE have many sites with petroleum hydrocarbons, chlorinated solvents, PCBs, and PAHs contaminating soil and groundwater. Bioremediation performed in-situ could be the lowest cost and least environmentally impacting approach to remediation, and the only practical approach in some cases.

This project has been identified as one of two initial priorities of the Remediation Technologies Development Forum, a collaborative effort of several large U.S. corporations, DOE, DoD, EPA, and academia. The forum is seeking to form specific consortia to address priority needs. If initiated through SERDP, this field facility would be the nucleus for a bioremediation consortium with potential future funding and joint research from all parties.

There is no existing comparable test-bed facility in existence today. However, the results from Wurtsmith will be closely coordinated with other individual field evaluation projects. Specifically, the research results from Wurtsmith will be providing needed data and information for application to the remediation of DOE, DoD, and Superfund sites.

There are approximately 43 distinct contamination sites in the Base. A hierarchy of site selection and scheduling will be established consistent with a priority of research and development needs and opportunities. A selection and scheduling rationale for the initial projects of the facility will be based on the needs and interests of specific clean-up scenarios



by the sponsoring organizations. Twelve sites have been identified preliminarily for research programs, and six that have pump and treat systems in place or designed would be the initial targeted research areas.

Initial research would stem from laboratory research currently conducted at the Great Lakes and Mid-Atlantic Hazardous Substances Research Center. Initial field studies would assess: the microbiological and biochemical factors affecting rates degradation; field engineering needed to duplicate laboratory results; and *in-situ* treatment of contaminated sediments.

A key first year activity is to establish the infrastructure at Wurtsmith (personnel, offices, equipment, etc.) to support future research activities.

**Expected Payoff:** There will be numerous clients for this facility, including those responsible for clean up of most National Priority List sites, state lead sites, Potentially Responsible Party sites, leaking Underground Storage Tank sites, and others. Users will include all levels of government—particularly DoD, DOE, state and local; industry and academic institutions.

There are many advantages to the use of bioremediation in hazardous waste site clean up. These include low cost, permanence, on-site application, low environmental impact, and good public acceptance. *In-situ* bioremediation could potentially save hundreds of millions in clean-up costs. It may be the only practical approach in some cases and offers an alternative to long-term pump and treat for groundwater.

This research facility will establish a key missing link between laboratory results and field results, enabling a much more rapid and extensive application of *in-situ* bioremediation.

The creation of this national facility by the federal government would also present an opportunity to establish a research consortium involving scientists in government agencies, private industry, and universities to solve problems and address narrowly focused issues. The Remediation Technologies Development Forum is particularly interested in a consortium for *in-situ* bioremediation research. Through this consortium, each of these parties would directly use the Wurtsmith research facility.

#### **Transition Plan:**

The EPA Superfund Program Office of Innovative Technology is an active supporter of this facility and will integrate results into the Superfund remedial action decision-making process, as will DoD and DOE. The results of the field research/demonstrations will be widely disseminated through the planned management consortium, the Bioremediation Action Committee, computerized bioremediation data bases, and through the private and government participants. Cooperative Research and Development Agreements and licenses under the Federal Technology Transfer Act will be used to ensure rapid commercialization.

<b>Funding: (\$K)</b>		<b>FY93</b>	<b>FY94</b>
1. Staffing/Program Development	***	300	100
2. Facility Development	***	2000	1000
3. Facility Maintenance & Staff Support	***	500	500
4. Field Research (SERDP Request)		1000	2000
<b>TOTAL</b>		<b>*3800</b>	<b>**3600</b>

\* EPA to provide \$500K.

\*\* The SERDP funding will be leveraged through subsequent funding for research at the facility by members of the consortium, if established. In addition, the State of Michigan has agreed to provide physical structures/buildings required for the facility, and the University of Michigan has offered cost sharing in the form of administrative personnel support.

\*\*\* Majority of funds allocated within the National DoD Environmental Technology Demonstration Program.

#### **Performers:**

Dr. Walter J. Weber, Jr., of the University of Michigan and current Director of the Great Lakes and Mid-Atlantic Hazardous Substances Research will serve as Project Director. A permanent staff (Director of field operations, field manager, office manager, technicians) will be hired.

Research projects may be performed directly by any participating party (university, company, agency, etc.) assisted by the permanent staff.

A Board of Directors and a Science Advisory Board will be established to help plan and oversee research activities conducted at the facility. These Boards will be comprised by representatives from each of the five HSRCs, the MDNR, the USEPA, the US Air Force, other Department of Defense representatives, the Department of Energy, and representatives of major categories of industry.

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\* Note: The SERDP Scientific Advisory Board provided specific guidance to this project. Their position statement on this effort may be found in a separate section within this document; see "Table of Contents."

## **SERDP Thrust Area: Installation Restoration**

### **Title: Organophilic Clay Biosorption Treatment of Low Level Plastizers and Solvents Contaminated Groundwaters**

#### **Problem Statement:**

The goal of this project is to develop a means of concentrating plastizers and chlorinated solvents onto an organophilic adsorbent(s); thereby, allowing cost efficient biodegradation of the concentrated adsorbates. Potential users include all groups, both private and governmental, that are involved in remediation of groundwaters contaminated with organic and explosives compounds.

The Department of Defense (DoD) and Department of Energy (DOE) have many sites that contain groundwaters contaminated with low levels of plastizers (acetone) and chlorinated solvents (trichloroethylene [TCE]). Current or traditional treatment technologies available for use in TCE treatment are granular activated carbon (GAC) and air stripping; however, neither technology results in the direct destruction of the organic contaminant. An innovative technology, ultraviolet (UV) chemical oxidation, will be available for use in the very near future for chlorinated solvent oxidation. Remediation costs for all of these technologies generally falls within the \$1.00 to \$5.00/1,000 gallons range. In the case of GAC, treatment of groundwaters containing low levels of chlorinated solvents becomes economically infeasible.

Acetone poses a very unique challenge to both traditional and innovative technologies. Acetone does not adsorb onto GAC due to its high water solubility. It does not strip in air strippers due to its low Henry's Law constant. It does not oxidize in chemical oxidation systems due to its stable chemical structure. It is biologically degraded, but biotreatment is inappropriate for treatment of low level contaminated groundwaters because an active biomass cannot be sustained due to the low substrate loadings. Unfortunately, most groundwaters contain acetone at relatively low levels. Expensive cometabolite addition is almost always required.

Both acetone and TCE can be biodegraded. Acetone is very susceptible to biotreatment using aerobic consortia. TCE is somewhat more difficult to biodegrade, but recent advances in cometabolic pathways (methanotrophic) indicate that biotreatment of TCE is feasible. However, one problem detected with TCE degradation is the tapering off of microbial destructive activity over time in continuous and semi-continuous biological systems.

Biosorption is almost always associated with GAC. It has primarily been used as a means of extending the service of a GAC bed by regeneration of the spent carbon within the bed. Recent work on phenolic compounds has resulted in the development of an innovative technology known as biofilters. This technology utilizes GAC as a means of structurally supporting an active biomass.

Organophilic clays (OPCs) are innovative adsorbents that have received limited evaluation and even less application. OPCs have been successfully used to remove low levels of wood preserving waste from contaminated groundwater. Results of this evaluation are encouraging, but disposal of the spent OPC is a problem.

The USAE Waterways Experiment Station (WES) has conceptualize a treatment system for low level contaminated groundwaters based on biosorption and bioslurry systems. The concept is that the contaminants are adsorbed onto the OPCs until all the adsorption sites on the OPC becomes spent. The spent OPCs are removed from the reactors, ground into small particles, then the adsorbed contaminants biologically degraded in a bioslurry reactor on-site. This converts OPC adsorption from a simple phase-change technology into an on-site destruction technology.

Tyndall AFB has been active in development of microbial consortia capable of effectively degrading TCE from contaminated groundwaters. This technology can be tailored to interact nicely with the conceptualize OPC biosorption schemes.

Relationship to Current R&D Efforts - The USAE Waterways Experiment Station (WES) under the Environmental Quality and Technology Program (EQT) is developing a means of biologically regenerating spent GAC. WES also plans to evaluate the use of OPCs for treatment of explosives contaminated groundwater. It is hoped that OPC biosorption can be used for treatment of the low level explosives contaminated groundwater.

Tyndall AFB is currently developing a bioreactor for treatment of groundwater contaminated with higher levels of TCE. The consortia developed in these efforts will be useful toward development of the OPC biosorption concept.

#### **Project Description:**

There has been little or no direct development of OPC biosorption. Some past efforts on bioregeneration of spent GAC containing phenolic compounds indicates promise for microorganisms to degrade adsorbed compounds.

A recent evaluation of OPCs for wood preserving waste treatment indicate the utility of OPCs for groundwater remediation. Unfortunately, there are few options for disposal of spent OPCs (and GAC).

Under US Environmental Protection Agency funding, the WES has demonstrated the feasibility of bioslurry systems for treatment of soils contaminated with plastizers and wood preserving wastes using pilot scale bioreactors. The soils in these studies did contain clay fractions.

Tyndall AFB has demonstrated the feasibility of biologically treating TCE using aerobic microorganisms. Much of this work has resulted in the development of microbial consortia that have excellent activity toward chlorinated solvents.

The overall objective of this study to develop a OPC based biosorption process. Development of this technology will in the case of acetone, provide environmental engineers with a practical means of treating acetone. With respect to TCE, this technology may eliminate the problem of TCE activity loss over time.

The technical approach for this project is to develop OCP biosorption into a fieldable technology for site remediation. It will be approached through a series of tasks detailed

below:

- a. Task I. Evaluation of OPCs for Acetone and TCE Adsorption. The adsorption capacity of OPCs for acetone and TCE will be evaluated using both adsorption isotherms and small columns. The capacity of both compounds will be compared to that achievable using GAC. This will ensure that the most effective adsorbents is used for both compounds. The impact of cosolvency with other selected organic compounds will be evaluated using adsorption isotherms.
- b. Task II. Evaluation of microbial activity toward adsorbed acetone and TCE. The ability of microbial consortia to desorb and subsequently biodegrade the adsorbed acetone and TCE from the OPC will be evaluated using laboratory batch systems. Much of this effort will be directed toward TCE biodegradation since acetone biodegradation is much more refined. Radiolabelled isotopes will be used to track the fate of TCE and possibly acetone during biotreatment.
- c. Task III. Bench Scale Bioslurry Studies. Bench scale bioslurry studies will be performed to determine process feasibility, verify reaction kinetics and pathways, and set pilot studies test matrices. The bench studies will be performed using five liter all glass reactors operated in batch mode.
- d. Task IV. Pilot Scale Studies. Pilot scale studies will be performed using 70 liter pilot bioslurry reactors. If required, a process gas management system may be used if off-gassing of TCE and the selected cometabolite is deemed problematic. These pilot scale studies will be performed in the field at two DoD sites.
- e. Task V. Draft Report. A report detailing the following will be drafted:
  1. Describe techniques on how to perform bench scale treatability studies used for process evaluation during Feasibility Studies (FS).
  2. Discuss process feasibility and potential limitations.
  3. Present the results from the bench and pilot studies.
  4. Summarize available full scale equipment availability.

The report will be very design and applications orientated. the report will serve as a handbook for implementation of OPC biosorption at other field sites.

Relationship to DoD/DOE Environmental Objectives - The information obtained from performance of this study will assist in meeting several DoD/DOE environmental remediation objectives. This work effort will result in the development of a contaminant-destruction technology applicable toward both chlorinated solvent and plastizer compounds. Specific identified user requirements to be addressed through performance of this work unit include:

1.I.1.f. Treatment systems for water contaminated with organic contaminants (A,N,AF)

1.I.1.g. Treatment systems for water contaminated with chlorinated and defense hydrocarbons (A,N,AF)

1.I.1.i. Technique to maximize contaminant withdrawal with minimum water treatment (A,N,AF)

1.I.1.h. Treatment system for water contaminated with mixtures of chlorinated solvents and hydrocarbons (A,N,AF)

Technical issues to overcome as identified to date are listed below:

- a. Determine if OPCs have appreciable adsorption capacities for acetone and TCE.
- b. Determine if bioslurry treated ground OPCs can be treated to levels that render them environmentally safe and regulatorally acceptable.
- c. Determine if process gas recirculation will be required for TCE biodegradation of the ground OPCs.

**Expected Payoff:**

OPC biosorption treatment will fill a gap that currently exists in terms of treatment of low level acetone contaminated groundwaters. OPC biosorption may eliminate problems associated with reduced TCE bioactivity over time. The actual economic benefit is difficult to ascertain due to the innovative nature of the concept. A conservative estimate is that the technology could be implemented at a cost range of \$1.00 - \$3.00 per 1,000 gallons treated.

**Milestones:**

Major milestones under this work effort are listed below along with respective fiscal year they will be completed.

	FY
Perform OPC and GAC adsorption studies	93
Perform bench scale evaluation of biotreatment of spent OPCs	93
Perform bench bioslurry study	93
Design and construct pilot system	93
Perform field pilot studies	94

**Transition Plan:**

This technology development will generally follow the typical transitional path detailed under DoD's EQT Program. Within two years, the technology will be transitioned from a bench concept to an implementable technology. Technical assistance will be available to technology users during design and implementation of OPC biosorption. The technology will be transitioned to the user community through technical papers, presentations, and the

work unit report.

**Funding: (\$K)**

Previous Funding and Major Deliverables - No funding is planned in development of OPC biosorption under current research programs.

Proposed SERDP Funding - The proposed funding requirements by agency and FY are listed below.

Per Agency by Task	FY93	FY94	Total
I. Bench Adsorption Studies	125	0	125
WES	125	0	125
Tyndall AFB	0	0	0
II. Bench Microbiology Evaluation	125	0	125
WES	0	0	0
Tyndall AFB	125	0	125
III. Bench Bioslurry Studies	200	0	200
WES	150	0	150
Tyndall AFB	50	0	50
IV. Pilot Studies	50	400	450
WES	50	300	350
Tyndall AFB	0	100	100
V. Report	0	50	50
WES	0	25	25
Tyndall AFB	0	25	25
Organizational Totals			
WES	325	325	650
Tyndall AFB	175	125	300
Overall	500	450	950

**Performers:**

The performers for this work unit are USAE Waterways Experiment Station and Tyndall AFB.

Advice from OPC manufacturers will be incorporated into the final technical approach for this study. Their knowledge of their product will be invaluable.

The EPA's Technology Innovative Office (TIO) has expressed interest in maintaining contact on the development of this technology due to its very innovative nature.



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## **SERDP Thrust Area: Installation Restoration**

**Title:** Treatment of Process Off-gases Contaminated With TCE Using In-Situ Soil Based Aerobic Bioreactors

### **Problem Statement:**

This field demonstration will generate cost and effectiveness data for an innovative biotechnology for treatment of TCE contaminated off-gas streams produced from treatment systems such as air strippers. The targeted Departments/Organizations are the Department of Defense (DoD) and the Department of Energy (DOE).

The DoD and DOE have sites that are contaminated with chlorinated solvents such as trichloroethylene (TCE). Remediation processes used in treatment of TCE contaminated soils and groundwaters (i.e. air stripping, soil vacuum extraction, and low temperature thermal treatment [LT<sup>3</sup>]) result in the generation of TCE contaminated gas streams. Recent regulatory trends require treatment of these contaminated off-gases. Development of a biologically based off-gas treatment system would convert air stripping, which is a commonly used treatment process, from a simple contaminant phase-change process to an on-site contaminant destruction process without significant cost increases.

The U.S. Environmental Protection Agency, Robert S. Kerr ERL (RSKERL) Ada, Oklahoma discovered and patented an innovative biotechnology for remediation of TCE contamination. Their discovery was that natural bacteria in soil that degrade a variety of gaseous alkanes (such as natural gas, propane, or butane) will fortuitously degrade TCE under aerobic conditions. The process is well documented in the laboratory, and is ready for field scale evaluation. Process off-gases containing TCE vapors will be amended with gaseous hydrocarbons, and circulated through the vadose zone above a TCE spill. After acclimation, the soil will behave as a extended-residence time bioreactor.

A single DoD site will be selected for performance of the demonstration study. One potential site, Picatinny Arsenal, has soils that have a high degree of pertinent microbial activity. This work was performed by the US Geological Survey through an IAG from the RSKERL. The kinetics of depletion were similar to those exhibited by soils of similar texture collected from other parts of the U.S.

This is a new project for SERDP, following up on previous work supported by the RSKERL.

### **Project Description:**

The objective is to develop and demonstrate the innovative biotechnology to the point that it is competitive, in terms of cost and performance, with conventional process off-gas treatment technologies such as activated carbon.

A prototype soil-based bioreactor will be set up on-site. The bioreactor will either be an in situ system installed in the vadose zone with sheet piling for containment or an above-ground fully enclosed system. The actual bioreactor configuration installed at the site will be determined based on site conditions and regulatory requirements. The bioreactor will be

used to treat TCE contaminated off-gases from an active air stripper. Operational parameters will be varied systematically to evaluate the effects of air residence time, the chemical nature of the gaseous alkane substrate, the concentration of substrate, the concentration of TCE, the concentration of dichloroethylenes and vinyl chloride (which are traditional oxidation intermediates of TCE oxidation), and nutrients. After operational parameters have been optimized for TCE biodegradation, the prototype will be operated through a complete annual cycle to document its operational stability.

For benefit of direct comparison, the performances of two abiotic, commercial off-gas treatment systems, activated carbon and photocatalytic destruction, will be concurrently operated using the same influent gas stream. This effort will serve as a side-by-side comparative study of the two available technologies to the innovative biologically based process developed by RSKERL. The economics, operational histories, and effectiveness of each process will be evaluated and reported.

The following are tasks associated with the project:

- 1) Select test site (DoD installation)
- 2) Design bioreactor
- 3) Spec and purchase commercial treatment systems
- 4) Construct/install systems
- 5) Operate treatment systems
- 6) Compare performance of systems
- 7) Evaluation/Report

The USEPA (Gulf Breeze ERL) is developing a similar biotechnology for groundwater using organisms that degrade aromatic hydrocarbons. Their process works through a different enzymatic pathway. DOE/Savannah River Laboratory/Westinghouse are evaluating the use of the RSKERL technology in conjunction with lateral wells and air sparging. The USAF has supported work at Battelle Northwest Laboratory. DOE has supported work at Oak Ridge National Laboratory using USEPA-RSKERL technology in above-ground bioreactors. The WES is currently evaluating the feasibility of both the methanotrophic and aromatic pathways for treatment of TCE contaminated soils using bioslurry reactor equipped with process gas recirculation. Cornell University under contract to WES is developing an above-ground filter for treatment of TCE contaminated gas streams. This work differs from the proposed work in that it relies on a capture system followed by aerobic biodegradation.

The design of the bioreactor must contain the injected hydrocarbons and TCE vapors to prevent migration off site. The design must also eliminate explosion hazards.

#### **Expected Payoff:**

TCE in groundwater is currently pumped and treated by carbon adsorption or by air stripping. Air stripping is usually the process of choice because activated carbon is more expensive. Today's regulatory environment requires treatment of the off-gases emitted from the stripping unit. Three technologies have been employed. They are activated carbon (by far, the most popular), photocatalytic oxidation (an recently developed commercial technology), and thermal destruction (usually cost prohibitive). The optimized bioreactor should cost

less to build and operate than these conventional technologies.

#### Milestones:

	FY
1) Select site	93
2) Design bioreactor	93
3) Purchase abiotic systems	93
4) Install systems	94
5) Operate systems	95
6) Evaluation/Report	96

#### Transition Plan:

The RSKERL and the USAE Waterways Experiment Station (WES) will design the bioreactor. The CETHAMA will coordinate the siting of the pilot systems at an Army installation. The US Geological Survey, under an IAG from the RSKERL, will operate the treatment systems with assistance from the RSKERL and WES. The US Air Force, Tyndall AFB (USAF) will provide technical assistance to the overall project. The USEPA, USGS, USAF, and WES will evaluate the relative performance of the treatment systems. The RSKERL will have the lead in evaluation of the bioreactor system. All work unit partners will assist in technology transfer.

The design of the system will use materials, approaches, and techniques currently in use for bioventing of fuel spills. Contractors with experience with bioventing should not have difficulty with the technology.

#### Funding: (\$K)

Per Agency by Task	FY93	FY94
Select Site	55	0
RSKERL	15	0
USAF	5	0
WES	5	0
CETHAMA	30	0
Design Biofilter	250	0
RSKERL	150	0
USAF	50	0
WES	50	0
CETHAMA	0	0
Spec Abiotic Systems	20	0
RSKERL	0	0
7USAF		0
WES	20	0
CETHAMA	0	0

Install Systems	0	330
RSKERL	0	70
USAF	0	10
WES	0	200
CETHAMA	0	50

Organizational Totals		
RSKERL	150	70
USAF	55	10
WES	75	200
CETHAMA	30	50
Overall	310	330

**Performers:**

The performers are the USEPA-RSKERL, USAF, USGS (under an IAG to USEPA), WES, CETHAMA. The U. S. EPA currently holds the patent on the biofilter technology.

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## **SERDP Thrust Area: Installation Restoration**

**Title:** PCB Decontamination Using Base Catalyzed Decomposition Processes (BCDP)

### **Problem Statement:**

The goal for this project is to demonstrate a second generation Base Catalyzed Decomposition Process (BCDP). This modified system will be more cost effective for remediating PCB contaminated media. The Department of the Navy is the primarily targeted department. There are thousands of Navy, DoD, DOE and EPA sites being identified for PCB contamination in all types of media, liquids and solids. The current remedial techniques are ineffective, either technically or financially. Incineration is too expensive, and ash disposal may create problems due to its containing dioxin and furans; landfilling is impractical, from a long term liability standpoint; and bioremediation procedures for PCBs are not available. Although recent developments in bioengineering techniques show some promise, they will take 10 or more years to be usable in the field; when considering permit licensing, mass production of cultures, and engineering design and application. This proposed project will overcome all these barriers. This is considered a technology extension RDT&E effort beyond the currently DERA funded Guam project.

### **Project Description:**

The objective of this project is to conduct RDT&E to modify, automate and perfect an effective technological procedure and process, for remediating PCB-contaminated media. The BCDP is a chemical dechlorination method for PCB decomposition using inexpensive and non-toxic baking soda under a low temperature. A 1-2 ton per hour BCDP system has been fabricated for testing at Public Works Center (PWC), Guam. Sampling, data analysis from the test bed operation could identify shortfalls and required modifications. Further RDT&E effort will bring in a perfected, fully automated, cost-effective PCB decontamination system.

The development of the second generation technology will be carried out by NCEL, and will involve EPA Risk Reduction Engineering Laboratory (EPA/RREL), DOE Pacific Northwest Laboratory (DOE-PNL), and some universities and industries.

### **Expected Payoff:**

Application of the second generation PCB decontamination system will reduce costs by a factor of 10 when compared to incineration. This process will also reduce long term liability for the Navy, DoD, DOE, and EPA. Therefore, it will become a widely used technology for handling PCB problems.

### **Milestones:**

DERA Funding:  
Complete PCB Soil Treatment at PWC Guam

FY  
94

**Proposed SERDP Funding:**

Sampling, Data Collection and Analysis of the Testing System operation at PWC Guam	93
Conduct Additional Lab and Field Testing for Necessary System Modifications Identified	94
Prepare Design Specs for a Second Generation PCB Decontamination System-1/2 per hour to 1/4 ton treatment capacity	94
Prepare Technology Transfer Package and Assist in Technology Implementation	95

The projected accomplishment for the execution year is to complete sampling, data collection, and analysis of the BCDP Test Bed operated at PWC Guam, and also to initiate additional lab and field testing for necessary system modifications identified.

**Transition Plan:**

The final Technology Transfer Package for the modified, fully automated PCB decontamination system will be transitioned to DoD and other agencies by the end of FY95. Industry can then readily apply the technology to remediate all PCB contaminated media to meet regulatory requirements.

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
400	200

**Performer:**

The performers will be Navy/NCEL, EPA/Risk Reduction Engineering Laboratory (RREL), DOE - PNL, as well as universities and industries.

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## SERDP Thrust Area: Installation Restoration

### Title: Demonstration of Enhanced Source Removal for Aquifer Restoration

#### Problem Statement:

The goal of this project is to provide field demonstrations of processes to remediate aquifers contaminated by nonaqueous-phase liquids (NAPLs) and other contaminants in a timely and cost-effective manner.

These demonstrations are targeted at DoD, DOE, EPA, their contractors, and other public and private organizations responsible for remediation of contaminated groundwater.

Low-solubility organics, such as chlorinated solvents, were used and released to the environment in massive quantities during the 1950's, 60's and 70's. These contaminants have migrated through the subsurface and entered groundwater at over 1,000 DoD sites. At these sites the organic contaminants are found in one of three phases: (1) dissolved in the groundwater (dissolved phase), (2) sorbed to the aquifer solids (sorbed phase), or (3) as a separate nonaqueous phase liquid (NAPL phase), all of which need to be removed if the groundwater is to be restored to a usable quality.

The limiting factor to satisfactory remediation at over 75 percent of the hazardous waste sites in the United States is restoration of ground-water quality. For those contaminants that have found their way into groundwater in the deeper subsurface, and are beyond the reach of excavation or other surface treatment, remediation technology options are extremely limited. The technology chosen at over 90 percent of the sites with contaminated ground water is extraction followed by surface treatment. This technology, commonly known as *pump-and-treat*, has had some success in containing contaminant plumes and removing dissolved-phase contamination in relatively homogeneous geologic formations, but, as currently implemented, has not proved to be generally effective at restoring contaminated ground water to desired levels of cleanliness.

The major limitations to the successful use of pump and treat are related to difficulties in extracting contaminants from the subsurface. While research is still needed to optimize surface treatment of the extracted groundwater and contaminants, surface treatment is a much more mature technology and is usually available once the extracted water reaches the surface. Characteristics of contaminated aquifers that are important in limiting the success of pump-and-treat include: (a) aquifer heterogeneity, (b) sorption of the contaminant to aquifer solids, and (c) the presence of a separate immiscible nonaqueous-phase liquid. These same problems plague other *in-situ* remediation technologies, such as bioremediation.

There is a particular need for enhancements to pump-and-treat technology that can overcome the limitations imposed by aquifer heterogeneity, sorption, and the presence of NAPLs. A number of enhanced pump-and-treat technologies have been proposed and demonstrated in the laboratory, but none have been subject to an objective evaluation in the field, nor is engineering design guidance available to allow their routine application to remediation of contaminated groundwater.



## **Project Description:**

The objective of this research is to demonstrate processes for enhancing contaminant removal (enhanced pump-and-treat technologies) in a variety of geologic settings and to produce guidance documents for applying these processes to remediate contaminated groundwater. The guidance will address the entire remediation effort, including site characterization and supporting laboratory work required to achieve the maximum benefit from the remediation technologies included in the study.

The proposed work will be a series of field demonstrations of enhanced pump-and-treat technologies supported by site characterization and laboratory research required to produce a credible field demonstration. The work will focus on remediation of sites believed to be contaminated by nonaqueous phase liquids (NAPLs), such as chlorinated solvents, although other important contaminant classes will be included by necessity. The proposal is to conduct these demonstrations at contaminated DoD sites to increase the likelihood that the result will be directly applicable to actual remediation projects.

The processes will be demonstrated at different sites with different chemical mixtures to determine their performance under a variety of conditions. Initial demonstrations will be in relatively homogeneous subsurface formations, with conditions that are believed to be the most favorable for successful remediation, to ensure that the technologies work in simple systems. This procedure will also reduce the number of factors that can confound the interpretation of the results. Some of this initial work has been included in current programs at both organizations.

The enhanced effort that forms the bulk of the work in this proposal is to demonstrate the processes at additional sites where the soil type or geologic formation is more complex (e.g., thin layers of clay or silt intermingled with sand), or the contaminant distribution makes access to the contaminant more difficult. Each of the technologies to be demonstrated is potentially applicable to more than one class of contaminants, and the proposed work will include the demonstration of the technology for different types of contaminants, as well as mixtures of contaminants.

The tests will be conducted as small-scale field projects. Each technology will be compared with one or more alternative remedial technologies, such as conventional pump-and-treat. The results of these comparisons will show the differential improvement achieved by one process relative to another. If a suitable site can be made available, several technologies will be compared at one time under the same conditions.

The proposed work will demonstrate processes to enhance subsurface contaminant removal that are presently, or soon will be, at a stage of development where they can be seriously considered for use in installation/restoration programs at DoD facilities, as well as by other federal, state, and private organizations responsible for remediating contaminated groundwater. Such processes include innovative methods, like pulsed pumping, to optimize system design and operation for conventional, as well as enhanced pump and treat; solvent flushing with water-miscible solvents such as ethanol; surfactant flushing; hot water flushing; and methods for forcing fluids through regions of low hydraulic conductivity.

Each evaluation will involve a set of similar tasks, which are:

- Laboratory testing
- Site selection and characterization
- Design and construction of test facility
- Operation and monitoring
- Evaluation and reporting

Each of the processes to be demonstrated in the proposed study has been shown, in laboratory studies, to overcome some of the limitations that prevent the timely and cost-effective remediation of contaminated aquifers. However, there are a number of factors that are not evaluated by laboratory tests, that are poorly understood, and that will have a bearing on the success or failure of these field demonstrations. Three of these factors are: the high degree of spatial variability in the typical subsurface environment, the difficulty of bringing about *in-situ* mixing of a remedial additive with a subsurface contaminant in the absence of turbulent flow, and changes in the hydraulic properties of the system as the NAPL is removed. These factors will be accounted for in the system design, but they have the potential to impact the success of the demonstrations.

#### **Expected Payoff:**

The demonstrations will provide guidance in the application of these technologies based on carefully documented field experience, which should, in turn, improve acceptance of the tested innovative technologies within the regulatory community. Estimated costs for groundwater remediation by DoD and other federal agencies range upwards of hundreds of billions of dollars, and even incremental improvements in efficiency will justify the costs of the proposed research.

#### **Milestones:**

Select test sites and technologies for first set of tests	FY93
Initiate site characterization and project design for first set of tests	FY93
Construct and install treatment system for first set of tests	FY94
Initiate first set of tests, collect and analyze operational and monitoring data	FY94
Select test sites and technologies for second set of tests	FY94
Conduct site characterization and project design for second set of tests	FY94
Construct and install treatment system for second set of tests	FY95
Initiate second set of tests, collect and analyze operational and monitoring data	FY95
Complete data collection for first set of tests and write test reports	FY95
Complete data collection for second set of tests and write test reports	FY96
Produce summary report for all tests	FY96

#### **Transition Plan:**

The proposed work will consist of relatively small-scale controlled field demonstrations of subsurface remediation technologies. This enhanced demonstration program will speed up the transition to implementation by providing needed additional information on the capabilities of each enhanced remediation process under a variety of field conditions. The reports and guidance documents resulting from this work will be written such that they will

be suitable for planning implementation at larger field scales.

The EPA/RSKERL Technology Support Center (TSC) has provided technical assistance on over 300 Superfund sites since 1987. RSKERL has conducted numerous technology transfer seminars for EPA regional personnel, state personnel, and private contractors who are responsible for subsurface remediation at hazardous waste sites. In addition, RSKERL is currently involved in evaluation of pump-and-treat remediation projects for the Air Force. The TSC will provide a very effective means for transferring the results of this research to the user community. The AFCESA is integrated into the Air Force Installation Restoration Program through the Air Force Center for Environmental Excellence and the Army Corps of Engineers, which provides a direct connection between the results of their research activities and the subsurface restoration community.

Subsurface restoration practitioners should be able to make direct use of the results of these demonstrations. The results will also be directly applicable to the needs of the regulatory community and are expected to promote the acceptance of innovative technologies for subsurface remediation.

**Funding: (\$K)**

	FY93	FY94
Site Selection and Characterization		
DoD-AF		
EPA/RSKERL	300	250
	700	550
System Design and Construction		
DoD-AF	350	250
EPA/RSKERL	850	550
Operation and Monitoring		
DoD-AF	--	300
EPA/RSKERL	--	700
Evaluation and Reporting		
DoD-AF	--	--
EPA/RSKERL	--	--
Totals by Agency		
DoD-AF	650	800
EPA/RSKERL	1,550	1,800
Overall Totals	2,200	2,600

**Performers:**

The performers for the proposed work are: EPA—Robert S. Kerr Environmental Research Laboratory, Ada, OK; University of Florida, Gainesville, FL; DoD (Air Force)—Civil Engineering Laboratory, Tyndall Air Force Base, FL; Surfactant Associates, Oklahoma City, OK; University of Waterloo, Waterloo, Ontario; Duke University, Durham, NC; and the Air Force Institute of Technology.

The Environics Laboratory is currently involved with Surfactant Associates of Oklahoma City, OK, who are working with surfactants to solubilize and mobilize DNAPLs. RSKERL has a contract with GeoTrans of Sterling, VA, which is in the process of completing a guidance document for evaluating and characterizing sites believed to be contaminated by DNAPLs. Other opportunities for industrial involvement will be identified as the work progresses.

Cooperative agreements with academic and research organizations already involved in development of aquifer remediation technology will be used to conduct part of the proposed research. CRDAs will be developed as the project progresses.

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## **SERDP Thrust Area: Installation Restoration**

**Title:** In-Situ Abiotic Degradation of Solvent Contaminated Groundwater

### **Problem Statement:**

Discharges of chlorinated solvents to subsurface environments has led to contamination of groundwater resources. Cost-effective remedial alternatives for contaminated groundwater must be explored. The current common practice is to pump the contaminated groundwater and treat it above ground. This has proven to be expensive due to capital costs, maintenance, and the long time required for aquifer cleanup. Engineering a suitable environmental in situ to enhance aerobic biodegradation of contaminants in the water saturated subsurface has generally proven difficult. Contaminant source cleanup technologies generally leave sufficient residual contamination to require additional groundwater remediation efforts. Remediation of sites contaminated with dense non aqueous phase liquids has proven difficult due to their ability to sink below the water table, thus preventing effective source cleanup.

### **Project Description:**

The technical objective of this project is to determine the abiotic oxidation and reduction reactions of contaminants which may be enhanced in the subsurface environment. Evaluate methods which may be used to enhance these abiotic degradation reactions in the subsurface.

Laboratory research will concentrate on metal porphyrins and redox proteins as reducing agents although others may be considered. Emphasis will be placed on anoxic systems since oxygen is generally depleted in contaminated aquifers. Methods for introducing the porphyrins or redox proteins to the subsurface will be explored. Methods to engineer the necessary conditions in the subsurface which will not adversely affect groundwater quality will be examined. Degradation of several common groundwater contaminants of Air Force concern will be placed on reduction of the chlorinated solvents, TCE, and PCE. This effort is a follow-on to "In Situ Contaminant Mobility Reduction Using Surfactants: (JON 19006002) and "Reduction of Chlorinated Organics in Groundwater" (JON 19007067).

This project is in the Air Force Environmental Quality Research, Development and Acquisition Strategic Plan and the Tri-Service Environmental Strategic Plan under DoD Pillar I: Cleanup; Requirement Thrust II: Treatment of Solvents in Groundwater.

Tasks identified to accomplish this goal include determining the potential oxidizing and reducing agents and to evaluate potential methods for emplacing the redox agents in aquifers. Also to evaluate conditions necessary to promote electron transfer between the redox agents and groundwater contaminants, as well as those necessary to regenerate to redox agents, and to evaluate potential methods for establishing the necessary conditions in situ for abiotic degradation reactions to occur.

### **Expected Payoff:**

The technology could provide a cost-effective remedial alternative for Air Force groundwater

contamination sites and reduce the associated liability. The IRP, MAJCOMs, contractors, and civilian environmental engineering community will use/sponsor this technology.

**Milestones:**

Emplacement of redox agent on aquifer material	Mar 93
Establish that suitable reaction kinetics can be obtained	Jul 93
Assess various emplacement method/redox agent paris	Aug 93
Final report	Sep 93

**Transition Plan:**

A 6.3 field demonstration will follow and utilize that system. Assuming success of the 6.3 efforts, further transition to the field will be coordinated with AFCEE and AFCESA program offices.

**Funding: (\$K)**

FY93  
700

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## **SERDP Thrust Area: Installation Restoration**

**Title:** Air Sparging and In-Situ Bioremediation Research and Demonstration at Picatinny Arsenal, NJ

### **Problem Statement:**

Bioremediation enhancement to air sparging technology may provide a cost effective strategy for removing trichloroethylene (TCE) and related chlorinated solvents from ground water. However, unresolved technical issues focus on quantifying the incremental benefit and designing efforts to stimulate microbial degradation. The overall goal of Phase I of this project is to develop laboratory and field methods for determining the effect of sparge gas composition on the partition of mass removal due to volatilization and microbial processes. The methods will be demonstrated at Picatinny Arsenal, New Jersey, a site with a well-characterized plume of TCE contamination. Phase II of the project will involve the design and operation of a full-scale sparging/bioremediation demonstration at Picatinny Arsenal based on the findings of Phase I. The overall project will resolve technical and institutional issues that inhibit operational use of the technology.

The subject technology will be implemented at a Department of Defense site, under regulatory auspices of U.S. Environmental Protection Agency and the New Jersey Department of Environmental Protection and Energy. The subject technology was developed under a Department of Energy program.

Air-sparging and coupled in-situ bioremediation has been implemented at the Savannah River site. The Savannah River Project was designed as a scientific demonstration. In addition, the site is characterized by specific geochemical conditions, most notably, the plume was aerobic. An anaerobic contaminant plume, like the one at Picatinny Arsenal, is perhaps more typical of TCE plumes, and introduces questions related to the rate of adaption of the microbial consortium and engineering considerations related to induced precipitates.

TCE is the dominant contaminant in a plume within an unconfined glacial aquifer at Picatinny Arsenal. The unconfined aquifer is about 50 feet thick in the vicinity of the contaminant plume. In 1991, the highest measured concentration of TCE was 21,000 micrograms per liter. In 1986, the site was selected by the USGS Toxic Substances Hydrology Program as its research site for chlorinated solvents. Research includes characterization of TCE, related contaminants, and contaminant geochemistry in the aquifer and the unsaturated zone and fate and transport evaluation. The army has initiated an interim action under CERCLA to contain and treat the plume by pumping before it enters Green Pond Brook. The potential for sorbed or non-aqueous phase TCE to act as a continuing source of contamination may necessitate that the pump and treat operation continue indefinitely. The enhanced sparging technology could mitigate this condition.

### **Project Description:**

The objective is to develop methods to quantify the total rate of removal of TCE contaminant for an air sparging remediation system adapted to enhance contaminant removal with aerobic cometabolism. The total rate of removal is the sum of a component due to physical stripping

(volatilization) and a component due to aerobic cometabolism which will both be determined to allow for an evaluation of the cost effectiveness of the microbial enhancement. The methods are to be demonstrated at an existing site of TCE contamination and in the laboratory with porous media collected from the site.

The workplan has three major components: (1) development of methods to conduct sparging/cometabolism laboratory experiments with contaminated sediment, (2) application of overall method to pilot scale experiments at Picatinny Arsenal, and (3) development of a mathematical model to analyze the transport of sparged vapor phase constituents from the water table to extraction wells for the purpose of determining the distribution of mass flux across the water table.

Site geochemistry will be monitored to assess initial conditions with respect to a wide range of inorganic and organic solutes. Initial site assessment will also include analysis of sediment cores to define lithology, total contaminant mass, physical characteristics, and selected microbial guild characteristics.

Laboratory experiments will be conducted with sediment collected during the site assessment described above. Two types of experiments will be conducted: closed system microcosm experiments and open system column experiments. The microcosm experiments will determine the feasibility of aerobic cometabolism over the range of anticipated geochemical conditions and methane concentration. The open column experiments will allow for emulation of the field experiments under controlled conditions. Cores of sediment taken from the Picatinny site will be instrumented for the columns. Control experiments conducted with pure nitrogen as the sparge gas will provide physical removal rate information to be compared with experiments conducted with sparge gases with various methane and oxygen concentration. These experiments will allow for quantification of the effect of varying design parameters on system performance. The information obtained for the Picatinny sediment will allow for the rational design of pilot-scale experiments.

Pilot scale sparging experiments will be conducted at Picatinny Arsenal within the well-characterized site. The purpose of these experiments is to apply the overall method in-situ and to demonstrate the scaling up of laboratory information and application of the mathematical model (discussed below). The experiments will be conducted with a single sparge well. Site geochemistry will be monitored to assess initial conditions. Initial site assessment will also include analysis of sediment cores to define the total contaminant mass for the porous media, physical characteristics and selected microbial guild characterizations. Mass removal rates will be calculated by collecting vapors with a vapor extraction well and analyzing the exhaust stream for a wide suite of vapors including TCE and related contaminants, methane as well as signature gases like carbon dioxide, oxygen, and hydrogen sulfide. The monitoring will allow for separation of removal into a physical volatilization component and into a microbial component inferred by stoichiometric relationship to signature gases. It is anticipated that the experiment can be repeated at the same location to study variable injection rates and methane loading after a time interval passes which allows for the recontamination of the sparged column from surrounding ground water. It is anticipated that pilot scale experiments can be by-passed in subsequent operational applications of the technology.



A Mathematical model of the vapor extraction process will be constructed to determine the spatial effect of the sparge well by allowing for the calculation of constituent-specific mass flux across the water table to the extraction well. Reactions that occur in the unsaturated zone while TCE, methane, and oxygen are in transit to the extraction well(s) will also be simulated. This model is currently under development at the USGS. It will be completed, applied, and published as a public domain code during this project.

#### Expected Payoff:

- 1) Development of methods for performance evaluation and development of design criteria for air sparging with bioremediation enhancement.
- 2) Demonstration of methods at a site with geochemical conditions different than previously investigated at Savannah River.

#### Milestones:

##### Phase I

	Year 1	Year 2	Year 3
Advisory Panel Review	*	*      *	*
Program Plan	s-> end		
Characterization/Instrumentation	s->	end	
Laboratory Experiments	s->		end
Field Experiments	s->		end
Report Preparation			s->        end

#### Funding: (\$K)

##### Phase I

	Year 1	Year 2	Year 3
USGS	502	453	163
U.S. Army Contractor	40	20	10
HSMRC	15	25	15
Total:	557	498	188

#### Performers:

U.S. Army - coordinate contractor procurement and regulatory compliance

U.S. Geological Survey - responsible for conducting Phase I research

Private Contractor - assist in the design of vapor extraction system and development of unsaturated zone transport model in cooperation with U.S.G.S.

Hazardous Substance - coordinate and chair expert advisory panel which will provide technical oversight

**Expert Advisory Panel**

Dr. Richard Brown - Groundwater Technologies Inc., Princeton, N.J.

Dr. Peter Jaffe - Dept. of Civil Engineering, Princeton University

Dr. Peter Lederman - Director, Center for Environmental Engineering and Science, N.J. Institute of Technology

Dr. Brian Looney - Westinghouse Savannah River, Aiken, S.C.

Dr. John Wilson - USEPA, Kerr Research Lab, Ada, Oklahoma

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## **SERDP Thrust Area: Installation Restoration**

### **Title: Groundwater Cleanup of Organic Contaminants (TCE/PCE) Using Methanotrophic Bioreactors**

#### **Problem Statement:**

The general objective of this project is to demonstrate innovative technologies with potential for application to the DoD and DOE-DP waste management program. The specific goal is to develop and implement an environmental project for demonstrating/evaluating the potential of bioreactor bioreclamation for cleanup of deep subsurface contamination from disposal of chlorinated hydrocarbons in unlined waste disposal facilities.

The targeted department/organization is DoD and DOE since chlorinated solvents were disposed of in unlined facilities at all manufacturing and maintenance sites operated by DoD and DOE. Virtually all sites were metals processing (including nuclear production) and metals degreasing operations, e.g., airports, air bases, dumped large quantities of these solvents on the ground over 40 or more years. Since these solvents have been found to be carcinogenic at low concentrations in drinking water maximum allowable concentrations in drinking water are as low as 5 ppb. Thus DoD/DOE, and virtually the entire industrialized world are faced with a very large number of chlorinated solvent contaminated aquifers that will be required (regulatory mandates) to be cleaned up to very low concentrations. Regulatory drivers for this activity are RCRA (40 CFR 264 & 265 Subparts F & G), CERCLA (40 CFR 300 1986 Amendments Section 122), and SDWA (40 CFR 141). Given this ominous task any technologies that more efficiently treat (destroy) the contaminate, are less expensive, and pose less risk to the environment or human health will be of tremendous value.

Since 1988 we have been working with the Gas Research Institute and US Air Force in a collaboration to develop Bioreactor Methanotrophic Treatment Technologies. This effort has been co-funded by DOE/WSRC and the Gas Research Institute. In addition, several companies have donated materials and equipment for this effort, e.g., Envirex. An advisory team for this effort includes experts from Air Force, EPA Kerr Lab, USGS, DOE, and several national labs and universities. To date we have accomplished the following major objectives: 1) Defined MTT culture parameters that control pollutant transformations, 2) Demonstrated that microbial consortia fed with propane or methane not only are able to degrade trichloroethylene but also tetrachloroethylene, benzene, toluene, xylene and several other toxic compounds, 3) Increased rates of biodegradation of TCE by more than 100 times through better understanding of MTT metabolism, 4) Proved compatibility of methanotrophic bacteria with high-rate reactor designs, 5) Reduced hydraulic retention time to below one hour, 6) Reduced methane demand by 80% to less than 1200 scf/lb TCE destroyed, 7) Achieved simultaneous removals of nitrogen and phosphorus in an expanded bed reactor, 8) Complete design of a pilot-scale MTT GAC-FBR system for field demonstration, and 9) Started a field demonstration of the US Air Force Trickle Filter Bioreactor. This final 2 year field demonstration has been brought to this point by more than 5 years on planning, basic research and financial investments by Gas Research Institute and DOE of more than \$5 million.

Recent studies have shown that anaerobic bacteria are capable of reducing chlorinated alkenes to vinyl chloride, carbon dioxide, hydrochloric acid, and water (Bouwer et al., 1981;

Vogel and McCarty, 1985). Other studies have shown that trichloroethylene, dichloroethylene and vinyl chloride can be mineralized by bacteria very rapidly aerobically, the process being a co-oxidation that is driven by methane (Fogel et al., 1986). Since most ground waters are aerobic and do not have large amounts of methane, either type of biodegradation occurring naturally is highly unlikely. This observation probably also explains, in part, the recalcitrant nature of chlorinated alkenes and alkanes in the environment. Several studies have demonstrated that, using methylotrophic bacteria, chemostats and batch reactors can be utilized to degrade chlorinated alkenes and alkanes (Bouwer and McCarty, 1983; Vogel and McCarty, 1985). A complication of this bio-technology is the requirement of large amounts of methane and a strict aerobic environment. These conditions are costly and difficult to maintain under the large scale operations needed for aquifer decontamination. In addition, anaerobic utilization of trichloroethylene results in the formation and accumulation of vinyl chloride, which is mutagenic and recalcitrant (Vogel and McCarty, 1985). Thus anaerobic biodegradation may also generate another toxic substances. Our laboratory has just isolated and patented an aerobic heterotrophic microorganism capable of degrading trichloroethylene (Fliermans et al., 1988). In addition we have also demonstrated that microbial consortia isolated from contaminated subsurface sediments are capable of aerobically degrading trichloroethylene at much higher concentrations than the anaerobic digesters (Fliermans et al., 1988). Vinyl chloride did not accumulate with aerobic degradation, and methane or other special nutrients were not required. Our most recent work has demonstrated that a bioreactor driven by propane using a SRS consortium was not only able to degrade trichloroethylene but also tetrachloroethylene, benzene, toluene, xylene and several other toxic compounds (Niedzielski et al., 1989).

#### **Project Description:**

This project is concerned with the demonstration of a large scale continuous flow fermenter (bioreactor) for the treatment of trichloroethylene and tetrachloroethylene. Contaminated ground water will be pumped to the surface and into a large vessel containing ceramic and activated carbon particles with a biofilm of methane-oxidizing microbes capable of degrading TCE and PCE completely to carbon dioxide and chloride. This technology has the advantage of being on site degradation, terminal destruction, environmentally sound and cost effective. Cost effectiveness modeling has demonstrated that this technology will save at least 40-60% over conventional air stripping/activated carbon adsorption. Additional savings and effectiveness will be realized when compared to air stripping by the degradation of less volatile compounds by the bioreactor.

An objective of this project is demonstration of bioreclamation of contaminated ground water using a bioreactor. Indigenous bacteria from SRS subsurface sediments have been isolated that aerobically degrade chlorinated alkenes and alkanes to carbon dioxide, chloride, and water. The bioreactor technology task would involve an actual demonstration designed to:

- (1) confirm laboratory findings by operating bacterial microcosms in the field above grade,
- (2) scale up and validate use of large bioreactor at field site,
- (3) establish efficiency of such an approach for ground water cleanup and determine optimum operating conditions.

This task is divided into 4 major tasks:

Task 1 is to evaluate and test the USAF trickle filter design continuous flow fermenter

(bioreactor) under field conditions. Wells at the TNX pilot operations facility have been found to be contaminated with TCE and PCE. Water from these wells will be used to run field tests on the USAF bioreactor without leaving the pilot testing facility, thus providing excellent conditions for process optimization.

Task 2 will establish the efficacy of a multiphase bioreactor where the initial vessel of the bioreactor is anaerobic, followed by and aerobic methanotrophic treatment vessel. The efficiency of this process will be compared with the single phase system tested in task 1. Again the USAF bioreactor and TNX contaminated well water will be used for these tests.

Task 3 is to design and test a trailer mounted trickle filter continuous flow bioreactor that can further test concepts proven with the USAF bioreactor at a variety of field sites with different. The portability of this system will allow thorough testing at remote test sites. This pilot scale (1 gpm) system has been constructed and will be tested through FY93 under field conditions using a variety of operational conditions. Operational conditions will include ground water residence time, temperature, pH and contaminant concentration. In addition, several microbial inoculums (including SRS patented TCE degraders), nutrient compositions and biofilm substrate will be evaluated. Our patented technique for examination of bacteria from ground water will be used to monitor bioreactor conditions. We will also use new techniques to measure resiliency (phospholipid fatty acid analysis) with the aid of the University of Tennessee. ORNL personnel will assist in trickle filter design considerations and in initial operation.

Task 4 will consist of evaluating and testing a fluidized expanded bed design continuous flow fermenter (bioreactor) under a variety of field conditions to determine optimal configuration, feasibility, cost effectiveness, and efficiency of this technology for remediation of solvent contaminated ground water. The system will be operating at a contaminated site for two years to determine long term efficiency, resiliency of the biofilm, frequency of catastrophic biofilm events and cost effectiveness. Operation and capital cost and remediation effectiveness of this system will be compared to conventional technologies (air stripping) in use at the same site. This (2.4 gpm) system was constructed and hydraulic tested in FY92. Operation under field conditions using a variety of operational conditions can begin in FY93. Operational conditions will include ground water residence time, temperature, pH and contaminant concentration. In addition, several microbial inoculums, nutrient compositions and biofilm substrate will be evaluated. Our patented technique for examination of bacteria from ground water will be used to monitor bioreactor conditions. During FY91 and FY92 laboratory studies were conducted on bench top fermenters to determine design constraints by measuring microbial kinetics and mass transfer of the biodegradation reaction. These studies were used to determine the appropriate design for the pilot scale system. This task like the previous tasks is being co-funded by the Gas Research Institute.

#### **Expected Payoff:**

Successful demonstration of the technology in task 2, Bioreactor destruction of chlorinated hydrocarbons in ground water, will provide a cost effective and more environmentally acceptable method of ground water remediation. This has very wide application since chlorinated hydrocarbons are the most common contaminants found in U.S. drinking water. This technology can also be used for waste abatement and for remediation of other types of

hydrocarbon contamination, it has already been demonstrated that this system will simultaneously degrade toluene, xylene, and benzene.

#### **Milestones:**

Bioreactor Technology Demonstration is projected to take 2 years. Task 1. USAF Trickle Filter Bioreactor permitting and regulatory requirements have been met, and detailed test plans have been developed, along with QA/QC, health and safety plans, etc. The USAF Bioreactor is currently being demonstrated. Task 1 will require one year to complete, i.e. FY93. Task 2 will establish the efficacy of a multiphase bioreactor where the initial vessel of the bioreactor is anaerobic, followed by an aerobic methanotrophic treatment vessel. The efficiency of this process will be compared with the single phase system tested in task 1. Again the USAF bioreactor and TNX contaminated well water will be used for these tests. Task 2 will require 1 year for completion, finishing in FY93. Task 3 will utilize a mobile trickle filter bioreactor to test at remote field sites and will take 18-24 months, from FY93 into FY94 and will test further design constraints of the technology. Task 4, field testing of the fluidized expanded bed design bioreactor will require 18-24 months, from FY93 to FY94. Permitting and regulatory requirements will be met, and detailed test plans will be developed, along with QA/QC, health and safety plans. This task will verify laboratory findings for appropriate design and permitting.

#### **Tasks**

- 1 USAF Pilot Scale Bioreactor (10/1/92-9/31/93a)
  - 2 Anaerobic/Aerobic combined (10/1/92-9/31/93b)
  - 3 Mobile TF Pilot Scale Bioreactor (10/1/92-5/31/94c)
  - 4 FEB Pilot Scale Bioreactor (6/1/93-9/31/94d)
- a. Complete testing of USAF trickle filter bioreactor under field conditions.(Key)
  - b. Complete laboratory testing and evaluation of combined anaerobic/aerobic bioreactor combinations to increase rates and allow better PCE degradation.(Key)
  - c. Complete testing and evaluation of trickle filter design bioreactors with field trials from several areas under a variety of operating conditions.
  - d. Complete testing and evaluation of fluidized expanded bed design bioreactor with field trials from several areas under a variety of operating conditions.  
Full scale demonstration testing and evaluation. (Key)

#### **Transition Plan:**

Publication and presentation of reports and journal articles in peer-reviewed international scientific journals, DOE/DoD, national, and international symposiums will insure technology transfer. WSRC office of Technology Transfer will facilitate this further through patents, licensing seminars, etc. Gas Research Institute is also active in promoting this technology through seminars, brochures, etc.

**Funding:**

Tasks	FY93	FY94
USAF Pilot Scale Bioreactor	250	100
Anaerobic/Aerobic combo	100	0
TF Pilot Scale Bioreactor	300	100
FEB Bioreactor	700	800
OP	1350	1000
CE	300	300
Total	1650	1300

**Performers:**

DOE contractor at the Savannah River Site, Savannah Technology Center operated by Westinghouse Savannah River Company. Gas Research will be co-funding at \$500K or more, past funding was at the level of more than \$1 million/year since 1988. Other agencies involved in program include EPA, USAF, USGS and South Carolina Department of Health and Environmental Control. Industry participants include Envirex (donated reaction vessels), ECOVA, Man-Tech, and Radian. WSRC/DOE has a memorandum of understanding and bailment agreement in place for these bioreactor demonstrations with Gas Research Institute and Radian Corp.

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## **SERDP Thrust Area: Installation Restoration**

**Title:** Evaluation of the Semipermeable Membrane Device (SPMD) as a Passive In Situ Concentrator of Military Organic Chemicals in Water

### **Problem Statement:**

This project will provide the data required to evaluate the effectiveness of military organic chemicals in water which are likely to be accumulated through the food chain. Few methods currently are available to assess the time-weighted average contaminant load of low level persistent chemicals in water. These data are critical to provide meaningful assessments of potential ecological impact. The presence of lipophilic materials in water and subsequently in edible biological material is also a fundamental variable considered when calculating human risk estimates. This project is being proposed as a new project for the DoD in collaboration with an existing program of the U.S. Fish and Wildlife Service (USFWS).

### **Project Description:**

The SPMD has been developed by scientists at the National Fisheries Contaminant Research Center (NFCRC) of the USFWS as a simple, effective means of determining the level of biologically persistent chemicals in water. The device consists of a thin film of neutral lipid enclosed in a semipermeable membrane tube which is placed into the environment. Lipophilic compounds passively partition into the lipid through the membrane and are subsequently chemically analyzed after simple organic solvent dialysis. This technique is currently being used by a number of investigators to provide information on chemical concentrations at a variety of aquatic sites. The evaluation of the effectiveness of the SPMD to concentrate chemicals commonly found at military Installation Restoration (IR) sites is the first goal of the proposed project. Chemicals will be selected by a joint team of scientists from the NFCRC and the US Army Biomedical Research and Development Laboratory (USABRDL). The effectiveness of the SPMD as currently configured will be evaluated with munitions chemicals and their byproducts. Subsequent use of this technology in on-site IR applications will be accomplished in the Army's mobile biomonitoring laboratories by a combine team of USABRDL and NFCRC scientists. Chemical residue data from the SPMD will be used with USABRDL-developed hazard assessment bioassays to provide a more relevant integrated biological assessment of military sites.

### **Expected Payoff:**

The validation and application of the technology will provide an inexpensive and relatively rapid means of determining the level of bioconcentratable chemicals at IR sites. The data from these assessments will be extremely useful to risk managers in determining the nature and extent of these compounds at military sites, evaluating the effectiveness of remediation efforts, and will provide a useful tool for long term monitoring of the environment.



**Milestones:**

Select chemicals for evaluation FY93  
Begin Testing of munitions-related chemicals  
Complete munitions chemicals

Evaluate agent hydrolysis products FY94  
Begin field testing at IR sites  
Incorporate into monitoring program

**Transition Plan:**

Subsequent to testing and validation, the SPMD will be incorporated into the Integrated Biological Assessment package provided to users at Aberdeen Proving Ground and possibly Rocky Mountain Arsenal. Chemical selection will be coordinated with program managers at military sites to insure the relevance of the testing program. Technical reports and peer reviewed publications will reflect the USABRDL-NFCRC collaboration.

**Funding: (\$K)**

FY93	FY94
50	50

**Performers:**

The project will involve the personnel and facilities of the USABRDL and the NFCRC.

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**SERDP Thrust Area:** Installation Restoration

**Title:** Enhancing Bioremediation Processes in Cold Regions

**Problem Statement:**

The objective of this proposal is to improve remediation ability in areas subject to low temperatures. Due to limited resources, cost, and urgency of implementing solutions, on-site and easily implemented technologies, such as biotreatment, frequently are chosen for soil cleanup. The vast amounts of soil which are typically involved favor using large volume techniques that necessarily subject soil to seasonal temperature cycles. The net influence of freezing temperatures on the overall rate and extent of soil biotreatment is not sufficiently known to exploit or manage biotreatment systems in advantageous ways.

This is a new program that would enhance existing projects by providing basic research support. Substantial leveraging for field phases of this project is in place through existing and planned projects.

**Project Description:**

The scientific principles to be explored is the influence of prolonged low temperatures and extreme seasonal temperature changes on field bioremediation processes is a complex interaction of microbial and chemical rates, substrate-nutrient solubilities and availabilities, and physical-chemical phenomena driven by seasonal freezing. Rate adjustments based solely on traditional approaches, such as scaling from laboratory studies or  $Q_{10}$  values obtained from temperatures well above freezing without considering interacting phenomena encountered in field situations, may not realistically describe natural processes governing bioremediation in soils exposed to severe or repeated freezing. A preliminary conceptual model will be coupled with a series of laboratory experiments. Existing projects will be used to provide field data.

**Innovative Aspects:** Freezing and freeze-thaw influences on biological, chemical, and physical processes will be integrated. Combined laboratory and field studies will be used to provide feedback in both directions. Chemical structural activity relationships (SAR) will be used to select and group contaminants. Results will, therefore, be transferable based on structural activity relations rather than individual compounds.

**Potential Benefits and transition opportunities include:**

- a. Results are dual use and would readily transition to the public sector through field research and demonstration sites that are ongoing related projects.
- b. Increased knowledge would extend the operating season and potentially provide guidance for using natural freeze-thaw cycles to advantageously pretreat or provide additional on-site soil treatment.
- c. Project would provide knowledge base that is a prerequisite for developing root-rhizosphere based bioremediation technologies for tundra-covered soils.

- d. Envisioned benefits include in-situ treatment of contamination in the active zone of permafrost soils with minimal disturbance to permafrost or fragile surface ecosystems, as well as application in the northern tier of the continental US.
- e. Transition to arctic and subarctic sites, including Northern European and former Soviet Union sites, where conditions, location, available infrastructure, and cost preclude more intensive technologies, is highly feasible.
- f. Knowledge would support the dual-use technology of freezing containment by adding a cold-adapted bioremediation capability.

**Milestones:**

Define components of conceptual model of major freeze-thaw impacts on bioremediation	FY93
rates and endpoints (based on preliminary observations gained from ongoing projects)	
Evaluate importance of component processes in laboratory	FY94
Evaluate interactions of processes with SAR-grouped chemical classes	FY95
Compare field observations to laboratory based predictions	FY96
from ongoing (field data collected projects)	
Manipulate field systems based on gained knowledge (field systems from ongoing projects)	FY97
Evaluate altered field systems (ongoing projects will be leveraged to serve as field experimental sites)	FY98

Recent previous work in cold regions bioremediation primarily consists of:

- a. Private industry efforts using biopiles, treatment cells, and similar technologies. These efforts are minimally monitored with limited on-site or laboratory analysis. Documentation is sparse and restricted. Freezing effects are not addressed although treatment systems are subject to freezing.
- b. EPA efforts in EXXON Valdez cleanup. This was a coastal environment and subject to wave and storm action. CRREL has established a partnership with Gulf Breeze Environmental Research Laboratory.
- c. In-situ bioventing of lighter petroleum compounds in cold regions (Air Force), which focuses on subsurface, unfrozen soil systems. Extending the knowledge base could enhance the operation of bioventing to environmentally acceptable use in the active zone of permafrost soils. CRREL has a partnership with the Air Force.
- d. Ongoing related projects. CRREL is currently involved in developing treatment systems through partnering programs with Alaska Science and Technology, Alaska DOT, University of Alaska, FAA, Air Force, private industry, and CPAR projects. These projects are primarily applied research and demonstrations. CRREL is funded for 6.2 research on low temperature biotreatment. Support to address the knowledge gaps that these projects are identifying is needed.

**Performers:** CRREL has cooperative agreements in place with Alaska Science and Technology Foundation, EPA-Gulf Breeze Environmental Research Laboratory, Alaska DOT, FAA, RZA-AGRA, and the Air Force.

The amount of 6.2 and 6.3 leveraged funds from above sources through FY93 - FY95 is:

	(\$K)
AF25 (6.2)	575
CPAR (2 Projects)	800
FAA (3 Sites)	500
AF (1 Sites)	100

**Funding: (\$K)**

FY93	FY94
500	500

**Technical Point of Contact:**

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## **SERDP Thrust Area: Installation Restoration**

### **Title: In-Situ Immobilization of Heavy Metals in Apatitic Mineral Formations**

#### **Problem Statement:**

In situ immobilization of heavy metals and actinides into highly durable waste forms is not currently possible without the use of relatively expensive processes. Chemical stabilization is often used for immobilizing various heavy metal species, however, the waste forms frequently do not pass biotoxicity tests methods and the matrix created in the chemically stabilized waste forms has a short life span (tens of years) that can lead to increased rates of contaminant leaching. In addition, the presence of organics can often lead to formulation problems and can result in inadequate treatment. In conjunction with the on-going Keesler Air Force Base RCRA Facility Investigation Program, this proposed project will seek to demonstrate that heavy metals can be immobilized in situ with phosphates using commercially available mixing techniques to produce waste forms that have geologically long life spans (millions of years).

Phosphate minerals are formed in a wide range of environments from silicate melts, to oceanic margins, to natural soils, and to skeletal structures of organisms. Under normal conditions, most metals, lanthanides, and actinides have low solubilities and are readily removed from aqueous solutions during primary and secondary mineral formation. In the stable calcium phosphate mineral group of apatites, many cations readily substitute for  $\text{Ca}^{++}$ . Many phosphate minerals are stable over extraordinary range of chemical conditions. For example, hydroxyapatite is stable to temperatures of  $1000^{\circ}\text{C}$  and over a pH range from 2.5 to  $>13.5$ . In many instances, after incorporation into apatite, trace elements are retained and stable for hundreds of millions of years as shown by the detailed analyses of igneous and sedimentary environments as well through radiometric age dating using U-Pb and Nd-Sm isochrons obtained from fossil phosphate teeth and shells. In situ apatite mineral formation to stabilize heavy metal contaminated soils appears to provide significant improvement in simplicity of treatment and the resulting durability of the waste form compared to many current chemical stabilization processes.

This is a new SERDP project. The goals of this proposed project are to demonstrate that soluble phosphate solutions, introduced to heavy metal contaminated soils, will induce the co-precipitation of heavy metals into amorphous and/or crystalline phases of phosphate minerals (apatites) and that the resulting mineral structure has a durability and leach resistance that significantly exceeds the durability and leach resistance of chemically stabilized waste forms. This will be accomplished initially at a bench-scale on contaminated soils from Keesler followed by a pilot-demonstration at an IRP site such as Keesler or Eielson Air Force Base.

#### **Project Description:**

This project is structured to develop and demonstrate the capability to perform in situ immobilization of heavy metals via the introduction of soluble phosphates. The project scope is divided into two phases. The first phase involves analyses and speciation of heavy metals from sites at Keesler Air Force Base (soil samples have already been collected and are

available for analyses.) Soluble phosphate solutions will then be prepared for bench-scale testing. The resulting waste forms will be evaluated to determine the optimal phosphate solution composition for the conditions that exist at Keesler Air Force Base. Bench-scale testing will be conducted to determine the rates of reaction, thermodynamic solubilities, distribution coefficients and retardation factors for target heavy metals. A suite of standard waste form evaluation test methods will be conducted to allow for a quantitative comparison of the resulting apatite mineral form relative to performance standards specified by regulations and relative to the performance of other chemically stabilized waste forms. Using mineralogical and hydrochemical parameters of the subsurface environment, the waste form will be evaluated to determine its effectiveness in immobilizing the heavy metal contaminants and the ability of the apatite minerals to attenuate different groups of mobile ions.

Following a successful Phase 1, the second phase of the project involves working with an industrial partner to adapt existing in situ mixing and injection equipment and procedures to support the application of soluble phosphates and demonstrate the process at a pilot-scale in the field at Keesler Air Force Base on a contaminated soil site. Following the demonstration, the process and the resulting waste form will be evaluated to measure the durability and leach resistance of the resulting apatite minerals (waste form) relative to the bench-scale results. If the results are successful, the technology would then be transferred to the industrial partner and would result in a commercially available in situ stabilization process.

#### **Expected Payoff:**

The potential benefit of this project is the development of a superior in situ immobilization process for heavy metal contaminated soils. In addition to application to heavy metals, actinides and lanthanides also readily substitute with phosphates to form extremely stable minerals. Such a process would also be applicable to many Department of Energy and Department of Defense installations involving soils contaminated by radioactive chemical species. By developing the process in conjunction with an industrial partner, commercially available applications would be possible in the near term.

The impact this process would have relative to the current technology baseline of chemical stabilization methods would be to create an improved capability. The phosphate stabilized product would offer a waste form with a durability and leach resistance at least on an order of magnitude greater than waste forms produced from standard chemical stabilization agents. Additionally, current chemical stabilization methods require the addition of bulk chemical agents that can result in a 50% or greater volume increase. The injection of soluble phosphate solutions will not lead to appreciable volume increases.

#### **Milestones:**

Phase 1	After project start
1) Speciation of Metals from Keesler Air Force Base Soil Samples Complete	5 months
2) Soluble Phosphate Solution Formulation Complete	8 months
3) Bench-Studies and Waste Form Evaluations Complete	12 months

Phase 2	After project start
4) Cooperative Research and Development Agreement Established with Industrial Partner	8 months
5) Field Demonstration Operations at an ATC Base Complete	15 months
6) Field Demonstration Process and Waste Form Evaluation Complete and Final Report Issued	24 months

#### **Funding: (\$K)**

Phase 1 funding is anticipate to primarily consist of SERDP funds with some funding support from the Air Force Air Training Command (ATC) via the ongoing Keesler RCRA Facility Investigation. Phase 2 is anticipated to be jointly funded by SERDP, ATC and the Department of Energy.

	<b>FY93</b>	<b>FY94</b>
SERDP	350	625
ATC	50	100

#### **Transition Plan:**

Battelle, Pacific Northwest Laboratory's Waste Technology Center have the lead for this proposed work. During Phase 1, an industrial partner that provides chemical stabilization services will be selected to participate in the development of the process and support the Phase 2 field demonstration. By involving the industrial partner in the formulation, testing and demonstration, the industrial partner will attain sufficient knowledge to implement the techniques in the marketplace. This will help to provide the means for near-term industrial applications.

For the Phase 1 characterization and formulation and the corresponding Phase 2 demonstration, a DoD installation will be identified and a representative contaminated soils site will be selected.

#### **Performers:**

The proposed project will be managed by Battelle, Pacific Northwest Laboratory through Battelle's Waste Technology Center. Battelle operates the Pacific Northwest Laboratory for the U.S. Department of Energy. An Industrial partner that provides chemical stabilization services will be identified during the initial phase of the project and will participate in the development and field demonstration of the process to facilitate technology transfer. It is expected that a cooperative research and development agreement would be established with that industrial partner.

**Technical Point of Contact:**

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## **SERDP Thrust Area: Installation Restoration**

### **Title: Physical Separation Processes for Metal-Contaminated Soils**

#### **Problem Statement:**

As a result of industrial and military operations, large areas of land have become contaminated with heavy metals. Until recently only industrial facilities under RCRA and EPA CERCLA sites placed a key emphasis on metal-contaminated soil remediation projects. With the end of the Cold War, the projected reduction in military resources is leading to the return of more formerly used defense sites (FUDS) for public use. Both the Department of Defence (DoD), and the Department of Energy (DOE) are being impacted by the emphasis placed on the restoration of Federal lands.

In addition, the USEPA continues to strengthen regulation and enforcement regarding metal-contaminated soils and waters. Regulations, such as the national capacity variance (which expired in May, 1992) and the re-classification of military sites from active to inactive, are requiring a much closer look at metal-contaminated soils. The Clean Water Act restricts the quantities of metals that are permitted in groundwater. Also, there is a growing public awareness of metal toxicity in soils and water which has forced increased treatment and has complicated current disposal options. Such concern has led to a lowering of lead levels in drinking water and the restricted use of lead solder in plumbing systems. Regulations such as the RCRA Land Ban Restrictions, the Corrective Action for Solid Waste Management Units, and the Reauthorization of the Clean Water Act, coupled with the DoD and DOE facility closures are quickly necessitating the application of metals treatment technologies.

Unfortunately, current technologies only provide limited solutions to metal-contaminated soils problems. Presently, metals treatment technologies are limited. The two common ones are Dig and Haul, and Solidification/Stabilization (S/S). The land disposal restriction has severely limited the option of dig and haul technologies without S/S treatment (as a result of pre-treatment standards prior to waste placement in a RCRA-approved landfill.) On the other hand, S/S treatment does not remove the metal contaminants from the soil, thus, long term liability and future clean-up activities still exist. Also, S/S requires landfilling of the treated material generally in a RCRA-approved landfill. Landfill space is becoming more difficult to obtain and in the future, if landfill space is available, it will be more expensive to use. Thus, one cannot over emphasize the need to develop metal treatment technologies which remove the contaminants and reduce the reliance on landfills.

Generally few government agencies and almost no industries have devoted large amounts of funding towards research on metals contamination problems. The Navy (at the Naval Civil Engineering Laboratory [NCEL]) and the Army (at the U.S. Army Engineer Waterways Experiment Station [WES]) have recently initiated technology-based research to potentially provide treatment methods for metal-contaminated soils. Unfortunately, only limited funding is available for these efforts with the majority directed to address organic contamination problems. Funding of this SERDP project will greatly enhance the modest efforts currently underway at NCEL and WES and will result in the expansion of the Navy's current program well beyond their limited scope of small arms firing ranges.

## **Project Description:**

Metals generally associate with small size fraction particles in soils with high clay and organic matter content. If the large particles are separated from the smaller particles, a clean soil fraction may remain. This particle-size separation reduces disposal costs by reducing the mass of material requiring additional treatment. Military operations, such as small arms firing ranges and ammunition destruction, contaminate soils with large lead projectiles. In such cases, the large fraction of soil particles which are concentrated with contaminants, may also be separated and the metals concentrated for reuse. As a result, physical separation technologies offer a cost effective method of utilizing existing mining equipment and removing the fractions of soils which are enriched with metals.

The objective of this study is to evaluate and refine existing physical separation techniques to pretreat excavated bulk soils prior to secondary processing. This study will evaluate the potential of existing equipment for the removal and segregation of the portions of the soil containing heavy metals. Existing soil processing and separation equipment (such as spiral classifiers and hydrocyclones) will be evaluated. Metal-contaminated soil samples will be collected and a determination of the metals distribution and mobility in the soil fractions will be made. Equipment will be tested in the laboratory to determine the feasibility of the separation technologies using the individual unit operations. Based on the test results, various unit operations will be coupled to determine the optimal configuration (treatment train). When the optimal treatment system is determined, a mobile pilot unit will be constructed. This unit will be constructed with flexibility in mind to allow its use at as many sites as possible after the completion of this study. After the unit is constructed, it will be transported to two sites and evaluated for its effectiveness.

This study is divided into the following tasks:

I. Identification of Potential Sites: Various sites will be investigated with regard to their potential in demonstrating physical separation. Contaminated soil samples will be collected and characterized for subsequent laboratory screening and testing.

II. Laboratory Screening and Testing: The samples collected in task I will be separated according to particle size and density and analyzed for metal contaminants to determine the distribution of the metals in the soils. Based on these results, determination of the applicability of physical separation processes to the specific soils collected from the various sites will be made. Two soils showing a high potential for treatment will be processed through various physical separation unit operations to determine the most effective processes for additional evaluation. Unit processes will then be coupled to investigate the effectiveness of various treatment scenarios.

III. Mobile System Construction: This task simply consists of mounting the various unit operations on a mobile trailer facility, instrumenting the equipment and piping the equipment to allow maximum flexibility for evaluation.

IV. Field Testing: The mobile treatment system will be transported to two field sites and appropriate volumes of soil will be processed through the unit to characterize the performance of the system.

V. Analysis: Data collected from the field study will be analyzed to determine the operational problems with the system, the shortcoming of the treatment processes, the effectiveness of the treatment system, and the cost of the on-site pilot unit operations.

VI. Technology Transfer: It is critical to the success of this program that the information uncovered in the study is transferred to DOE, DoD, EPA, and industrial users. Funding is set aside for one individual to devote enough time to develop and implement technology transfer through project demonstration, facility visits, attendance and presentations at technical conferences, and the development of a video seminar.

VII. Final Report: A final report describing the results of the study will be prepared.

#### **Expected Payoff:**

Physical separation processes at their current state of development have a high potential to offer cost effective and implementable high volume throughput technologies for processing soils. Unfortunately, physical separation processes are limited to above-ground processing and could not be applied in situ. The volume of materials which required additional expensive treatment (i.e., incineration, extraction, vitrification) can be reduced by separating the contaminated fraction of soil from the clean soil. Clean soils may be backfilled without further treatment, thus reducing the volume of material which must be carried forward into other expensive treatment processes. Depending on how the contaminants are distributed in the soil, savings from 20% to 70% are expected.

Physical separation technologies offer the greatest possibility of near future full-scale implementation. The mining industry has utilized such technologies for a number of years. The difficulty with the efforts for metal removal in the mining field is that usually the processes are thought of as non-profitable once metal concentration in the ore is below about 1%. For environmental application most soils are contaminated with metal concentration at 1% or below. Thus, the use of physical separation techniques for environmental problems is regarded as a transfer of the mining methods to the environmental area. Mining research indicates that if physical separation techniques are effective for the soils in this study, these techniques should also be applicable to almost any contaminated soil where the contaminants partition into soil, fine, organic, or density phases.

#### **Milestones:**

Site Survey completed	Year 1
Laboratory Screening Completed	Year 1
Mobile Unit Constructed	Year 1
Field Testing Completed	Year 2
Final Report Completed	Year 3

#### **Transition Plan:**

Because many companies currently produce this equipment for mining technology application and have years of experience using this equipment, this technology should be easily transitioned to the private sector. Technology transfer is a key part of this project.

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
600	300

In addition, the following funding is available for leveraging:

	<b>FY93</b>	<b>FY94</b>
WES		
6.2 Physical Separation for Explosives Contaminated Soils	300	300
6.2 Physical Separation for Metal Contaminated Soils	100	200
NCEL		
Tech Demo - Rifle Range Mitigation	200	200

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## **SERDP Thrust Area: Installation Restoration**

### **Title: Peroxone Treatment of Explosives Contaminated Groundwaters**

#### **Problem Statement:**

The goal of this project is to develop a contaminant destruction technology that can treat explosives-contaminated groundwater at reduced costs compared to other technologies.

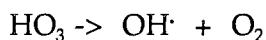
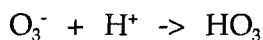
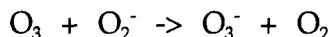
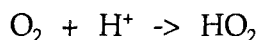
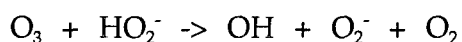
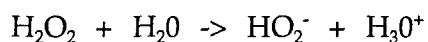
The Department of Defense (DoD) and Department of Energy (DOE) have many sites that contain groundwaters contaminated with explosives compounds. The current or traditional treatment technology available for use in explosives contaminated groundwater remediation is granular activated carbon (GAC). An innovative technology, ultraviolet (UV) chemical oxidation, will be available for use in the very near future under the DoD's Environmental Quality and Technology (EQT) Program. Remediation costs for both of these technologies fall within the \$1.00 to \$5.00/1,000 gallons range. UV/chemical oxidation is advantageous to GAC because it is a destruction technology and it does not produce a waste stream (i.e. spent GAC) requiring disposal. Also, unlike GAC, UV/chemical oxidation processes are still economically viable at relatively low groundwater concentrations. UV/chemical oxidation systems are often referred to as advanced oxidation processes because they result in the formation of powerful oxidizer species such as the hydroxyl radical.

Unfortunately, DoD installations requiring remediation of explosives contaminated groundwaters will require that GAC or UV based chemical oxidation systems treat literally millions to billions of gallons of groundwater. The cost to the DoD alone will be astronomical. Many environmental remediation engineers are hopeful that in situ technologies will one day completely replace pump-and-treat systems using above-ground treatment systems. Unfortunately, the technical truth of the matter is that above-ground treatment systems will always have a place in groundwater remediation activities. In-situ treatment will result in significant cost savings, but it is not a panacea. Not all sites or site situations are capable of supporting an in situ treatment system. More cost effective, contaminant destruction, above-ground based treatment systems are required.

Peroxone oxidation is a groundwater treatment technology that has great potential for treating contaminated groundwaters at reduced treatment costs. The main driving force in the development and presentation of this proposal is the potential cost savings that may be incurred with development of this technology.

Peroxone is a chemical oxidation process that has been used primarily for treatment of drinking water in both the United States and Europe. The process involves the addition of ozone ( $O_3$ ) and hydrogen peroxide ( $H_2O_2$ ) into a reactor system containing the contaminated groundwater. Peroxone generates hydroxyl radicals ( $OH^\cdot$ ) through the reaction of ozone with hydrogen peroxide. The hydroxyl radical is a powerful oxidizer that can destroy organic compounds into environmentally safe compounds.

The stoichiometric reactions that result in the generation of the radical during peroxone treatment are listed below,



Since the process does result in the formation of radicals, it is considered an advanced oxidation process (AOP). Peroxone does not require the addition of ultraviolet light to destroy organic compounds resulting in significant reductions in cost and ease of operation. Actual cost information obtained from French engineers indicate cost could even be as low as \$0.02 to \$0.10 per 1,000 gallons treated (for dilute concentrations). This represents an order of magnitude reduction of remediation costs as compared to traditional technologies such as activated carbon. Since peroxone does not require UV addition, operational problems associated with fouling of quartz tubes housing UV lamps are not of concern; thereby, eliminating a big operational concern and expense associated with UV based oxidation processes.

The USAE Waterways Experiment Station (WES) under the Army's Environmental Quality and Technology Program (EQT) has evaluated peroxone for treatment of trinitrotoluene (TNT) using bench scale reactors. Their results indicate that 100 ppb TNT can be removed to below detection limits within approximately 15 minutes of contact time. These kinetics are very competitive to those achieved using UV based systems that are more expensive to implement. No traditional oxidation intermediates have been detected in the test effluents.

The WES has also evaluated the feasibility of using peroxone for treatment of diisopropylmethylphosphonate (DIMP) and pesticides at Rocky Mountain Arsenal (RMA). Their results indicate that DIMP and the pesticides were effectively removed within the same approximate kinetic time span as the UV based systems. Studies evaluating reaction intermediates performed by US Army Biomedical Research Laboratory, under WES funding, indicate most of the DIMP is oxidized to inorganic phosphate. RMA has funded WES to perform a small scale pilot study during FY93 at the North Boundary Treatment System for removing DIMP and pesticides from the groundwater. A limited pilot system is currently under design by the WES staff. Some of the requested SERDP funding will be directed toward design and construction of a more complete pilot system. This "improved" system will have expanded capability for evaluation of the peroxone performance toward a variety of contaminants. The pilot system will be a mobile unit that can be transported to other installations for evaluation of peroxone for treatment of a variety of organic contaminants.

Finally, CETHAMA has plans for limited demonstration of peroxone for explosives contaminated groundwater remediation in FY94 and FY95. Unfortunately, the limited funding currently scheduled under the EQT Program will not allow for a complete evaluation of the process at multiple sites with differing explosives types and concentrations and water

matrices. It is important to note that oxidation treatment systems can be adversely impacted by poor water chemical matrices. One groundwater concentration may be very easily treated under one water matrix, but poor system performance could be experienced treating a different water matrix containing the same level of explosives.

### **Project Description:**

Peroxone has been successfully used world-wide as a drinking water treatment technology. Recent studies indicate that peroxone can effectively be used for removal of complex organic compounds, such as geosmin, pesticides, and chlorinated solvents, from drinking water sources. The results of these studies have stimulated a great interest within the U.S. for conversion of chlorine based water plants to peroxone systems. Chlorine drinking water disinfection systems tend to produce trihalomethanes (THMs) which are of concern due to their carcinogenic nature. The City of Los Angeles is currently constructing a 2,000 gpm peroxone system for drinking water treatment. Although, these efforts indicate promise for peroxone as a drinking water treatment technology, there has been little or no work in evaluation of peroxone as a site remediation technology (See the above section for current DA activities).

The overall objective of this study is to determine if peroxone is an aggressive enough technology for treatment of contaminated groundwaters which are much more complex and challenging to treat than drinking water sources. The development of peroxone into a fieldable technology for site remediation will be approached through a series of tasks detailed below:

a. Task I. Determination of Reaction Pathways and Kinetics. Since peroxone is a destruction technology, determination of the predominant oxidation pathway of selected explosives (TNT, RDX, HMX) will be determined using laboratory solutions of buffered distilled water and reagent grade target chemicals. Only single solute solutions will be used so additional carbon sources do not interfere with pathway determination. Kinetic parameters (at minimum, pseudo-first order rate constants) will also be determined. Analytical methods to be employed in determination of treatment pathways and kinetics will include high performance liquid chromatography (HPLC), stopped-flow spectrophotometry, and gas chromatography (GC).

b. Task II. Selection and Shipment of Groundwater Samples. Actual groundwater from contaminated military sites will be used in both the bench and pilot scale studies. This will ensure that the study remains focused on rapid field implementation. Candidate sites include Milan Ammunition Plant, Cornhusker Ammunition Plant, Sub-Base Bangor, and Hastings East Industrial Plant. Samples will be collected and shipped to WES for the bench scale studies. NOTE - All pilot studies will be performed on-site. Results from the bench testing will be used to design comprehensive pilot studies at a minimum of at least two DoD sites (one Army and one Navy). Obviously, sites used in the bench study will be carried through to the pilot level of effort.

c. Task III. Bench Scale Studies. Bench scale studies will be performed to determine process feasibility, verify reaction kinetics and oxidation pathways, estimate initial treatment cost estimates, and set pilot studies test matrices. The bench studies will be performed using one

liter all glass reactors operated in semi-batch mode with respect to ozone application. These studies will be performed at chemical oxidation laboratory of the Hazardous Waste research Center (HWRC) located at the USAE Waterways Experiment Station (WES).

d. Task IV. Pilot Scale Studies. Pilot scale studies will be performed using the mobile pilot system with 2.5 to 15 gallon per minute operating range. Four all-glass columns plumbed in series will serve as multiple contact chambers. The system will include several automated data collection systems that will be used to fully evaluate process feasibility in the field. At least two sites containing groundwater contaminated with explosives will be treated using the pilot system. This task will verify the results derived from the bench studies, evaluate process equipment, and refine cost estimates. The CETHAMA will be the lead agency in the conductance of this task.

e. Task V. Draft Application Manual. An applications manual detailing the following will be drafted for use by the user community in fielding the technology:

1. Techniques for performance of bench scale peroxone treatability studies - This information will ensure that engineering firms under contract to the installations will be able to properly evaluate peroxone during the FS stage of site remediation. The research team for this proposal will be available for consultation at any time during full field implementation to ensure a smooth transition of the technology from the research and development community to the user community.

2. Process feasibility and potential limitations - One important factor in development of any technology is a firm understanding of the limitations of the technology. The manual will detail all limitations and short-coming associated with implementation of peroxone that are identified. Close coordination with the user community will be maintained during the full-field application stage to further identify any additional limitations and problems as they occur. It is believed that the manual should be a "living" document that is periodically updated to ensure that corporate memory (DoD) is not lost during implementation at various sites. Lessons learned, whether good or bad, must be recorded so that other installations attempting implementation are keep fully abreast of new technical developments in order to ensure a higher potential for successful implementation.

3. Results from the bench and pilot studies - The results of both the bench and pilot studies will be presented in a concise and applications oriented manner. These results will be further transmitted to the user and regulatory communities. It is important that the regulatory community is completely confident that peroxone can be safely applied at DoD sites.

4. Summarize and assess cost estimates and full scale equipment availability - The manual will also include full cost estimates based on the results of both the RMA and EQT/SERDP demonstrations. An assessment of available equipment will be included to assist the design engineer in equipment selection. Basically, all equipment required for peroxone implementation are already available due to its operational history within the drinking water industry. This assessment of equipment will be oriented toward hazardous waste site remediation and the particularities associated with this unique technical and regulatory arena.



As stated above, the implementation manual will be very design and applications oriented. The manual will serve as a handbook for implementation of peroxone at other field sites. Peer review from other agencies such as the USEPA laboratories and COE design centers will be coordinated.

One final aspect of this effort will be the development of a DoD peroxone development team. This team will be multi-disciplined due to the complex chemistry, engineering, and regulatory environment associated with implementation of innovative technologies. The team will be headed by the USAE-WES and will consist of scientists and engineers from the Tri-Services, DOE, and the USEPA. The team will ensure that all project objectives are met and that the study remains streamlined toward rapid field demonstration.

The information obtained from performance of this work effort will assist in meeting several DoD/DOE environmental remediation objectives. This work effort will result in the development of a contaminant-destruction technology applicable toward both organics and explosives compounds, reduction of treatment costs, and improvements with site remediation operations flexibility. Specific user requirements to be addressed through performance of this work unit include (using the EQT format):

1.I.1.b. Technology for removal of energetics/other organics contamination (A,N)

1.I.1.f. Treatment system for water contaminated with organic contaminants (A,N,AF)

Technical issues to overcome as identified to date are listed below:

a. Ensure that the parent explosives compounds are oxidized into environmentally safe, non-regulated compounds.

b. Determine if peroxone can effectively treat contamination levels typically found at DoD/Doe installations as opposed to those levels that have traditionally associated with drinking water.

c. Determine the impacts of complex contamination matrices on treatment predicted from kinetic models.

#### **Expected Payoff:**

Potential users include all groups, both private and governmental, that are involved in remediation of groundwaters contaminated with organic and explosives compounds. Peroxone treatment will economically fill a gap that currently exist in terms of treatment of low level contaminated groundwaters. Although no funding is requested for the RMA pilot studies evaluating DIMP, pesticides, and aromatics removal, performance of this work unit will improve the overall quality of the RMA study by allowing RMA/WES to use an improved pilot system then could be developed on the RMA budget alone. In return, the RMA pilot studies (FY93) will allow for evaluation of the mobile pilot system in terms of mechanical performance prior to performing the explosives pilot studies in FY94.

Development of peroxone treatment will potentially reduce treatment costs by as much as an

order of magnitude. The degree of projected benefits are dependent on reaction kinetics and site requirements. Peroxone will offer environmental engineers and scientists a treatment technology that is flexible in terms of meeting treatment goals as groundwater influents change during site remediation. Elimination of UV light will reduce operational problems associated with quartz tube fouling. Finally, projected peroxone implementation costs indicate that savings derived from remediation of just one site with peroxone may recover all costs incurred during performance of this entire work effort.

#### **Milestones:**

Performance of this work effort will enhance existing research efforts under the EQT program by properly determining oxidation pathways of key compounds, allow evaluation of peroxone treatment systems at multiple sites with varying influent matrices, allow development of a mobile pilot system designed for performing research grade pilot studies yielding better definition of potential technology limitations and short-comings. In summary, this work unit will generally improve the understanding of peroxone capabilities and accelerate implementation of the technology, then if this work is performed concurrently with existing research plans under the EQT program.

Major milestones under this work effort are listed below along with the respective fiscal year they will be completed.

Task	FY Completed
Perform bench treatability studies	93
Design and construct pilot system	93
Determine oxidation pathways	93
Perform RMA pilot studies (RMA funding)	93
Perform explosives pilot studies	94

#### **Transition Plan:**

The proposed SERDP work will be an enhancement to the scheduled EQT work efforts without adverse impacts to the EQT schedule. The SERDP work unit proposed will be used to supplement economic short-comings within the EQT program and decrease the amount of time required to implement peroxone.

#### **Funding: (\$K)**

The proposed SERDP funding will be used to strengthen the overall peroxone development program under EQT. The additional funding will be used to improve the understanding of basic oxidation reactions, better definition of reaction kinetics, improve flexibility, transportability, and flow rate capacity of the planned pilot system, and fund performance of at least one additional pilot study. The proposed funding requirements by agency and FY are listed below.

Per Agency by Task	FY93	FY94	Total
Kinetics/Oxidation Pathway	250	50	300
WES	50	0	50
CRREL	200	50	250
Sample Selection/Shipment	30	0	30
WES	10	0	10
CETHAMA	10	0	10
Navy	10	0	10
Bench Studies	220	0	220
WES	200	0	200
CETHAMA	10	0	10
Navy	10	0	10
Pilot Studies	120	300	420
WES	100	50	150
CETHAMA	10	200	210
Navy	10	50	60
Report	0	50	70
WES	0	30	30
CETHAM	0	10	10
Navy	0	10	10
COE-Omaha District	0	20	20
Organizational Totals			
WES	360	80	440
CRREL	150	50	200
CETHAMA	30	230	260
Navy	30	60	90
Overall	570	420	990

**Performers:**

Partnering Department/Agency Laboratories - The research partners for this work unit are:  
 DA Agencies - USAE Waterways Experiment Station, USAE Cold Regions Research Engineering Laboratory, and USAE Army Toxic and Hazardous Materials Agency. DN Agencies - Navy Energy and Environmental Systems Agency.

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## **SERDP Thrust Area: Installation Restoration**

### **Title: Applied Demonstration Program in Environmental Compliance and Bioremediation Technology**

#### **Problem Statement:**

The goal of this program is to develop biological fluidized bed systems to biodegrade nitrates, chlorinated aromatic compounds, benzene, toluene, and xylene. The bed systems shall use granular activated carbon as the microbial support medium. The targeted departments/agencies are all DoD installations which have compliance and remediation problems with nitrates, chlorinated aromatic compounds, benzene, toluene, and xylene. The use of anaerobic expanded bed granular activated (GAC) bioreactors is an emerging technology for difficult-to-degrade organics. Bench-scale tests conducted by the U.S. Army Construction Engineering Research Laboratories (USACERL) have shown that biodegradation with anaerobic GAC contractors is a successful mechanism for removing dinitrotoluene (DNT) from influent wastewater. However, one effluent from the system contains high concentrations of Diaminotoluene. The USACERL is performing expanded bench-scale testing on actual DNT contaminated wastewaters at the Radford Army Ammunition Plant (RAAP), and the test results to date have been very encouraging. Data from bench scale testing shall be used by the U.S. Army Environmental Center (USAEC) to design and demonstrate a pilot-scale testing unit for further establishing optimum operating parameters and assessing economics. This program shall build upon previous efforts described above. The 1993 SERDP legislation specifies "that, of the funds provided under this heading, not less than \$3,500,000 of this amount shall be granted in fiscal year 1993 to a non-profit institution with expertise in applied environmental bioremediation technology, which includes experience in biological fluidized bed systems containing granular activated carbon as the microbial support medium, microbial cultures with proven ability to degrade nitrates, chlorinated aromatic compounds, benzene, toluene, and xylene, as well as an advance monitoring system to ensure optimal control of electron donor feeds, for the purpose of establishing an advanced process integration, scale up and applied technology demonstration program in environmental bioremediation technology."

#### **Project Description:**

The technical objectives of this program include the following: demonstrate that all environmental regulations can be met; demonstrate that all safety regulations can be met; provide comparative performance data to allow for selection of the most suitable technology by comparison with other technologies being developed; develop design data suitable for scale-up and demonstration; determine optimum operating conditions; determine the ability of the system to mineralize DNT to CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub>. Planning for the SERDP funding shall be done such that the SERDP program compliments the existing pilot demonstration by the USAEC as mentioned above. The recommended manner to accomplish this effort is for the USAEC and USACERL to jointly prepare a scope of work for the program and to solicit program work for competitive bidding. Per the SERDP legislation, the program work shall be awarded to a non-profit institution with expertise in applied environmental bioremediation technology. This institution shall establish an advanced process integration, scale-up and applied technology demonstration program in environmental bioremediation restoration

technology using microbial cultures to degrade nitrates, chlorinated aromatic compounds, benzene, toluene, and xylene. The approach described above shall be executed through a number of tasks that include: site selection; test plan preparation/review/approval; safety plan preparation/approval; environmental permitting; site preparation/equipment assembly; field demonstration; and technology transfer data package.

This technology is an innovative technology which permanently destroys the waste contaminant instead of transferring it to another medium such as granular activated carbon. The technology demonstration proposal discussed in this proposal is similar to the pilot scale demonstration using fluidized granular activated carbon beds to bioremediate DNT propellant production wastewater at the RAAP. The USACERL is performing expanded bench-scale testing on actual DNT contaminated wastewaters at the Radford Army Ammunition Plant (RAAP). Because the test results to date have been very encouraging, the technical risk using similar biological fluidized beds for other organic compounds are considered to be low to moderate.

**Expected Payoff:**

This technology will offer a destructive and cost efficient alternative to transferring the waste contaminants to carbon and/or other media.

**Milestones:**

FY 1993: Site selection, Test Plan Preparation/Review/Approval, Safety Plan Preparation/Approval

FY 1994: Environmental Permitting, Site Preparation/Equipment Assembly, Field Demonstration Technology Transfer Data Package

**Transition Plan:**

Testing data from the USACERL bench scale testing shall be used to design and demonstrate the USAEC pilot demonstration treating DNT and RAAP. Results from these studies shall be available for transition to the SERDP testing program.

**Funding: (\$K)**

FY93  
3,500

**Performers:**

The USAEC and USACERL shall work jointly to prepare a scope of work for the program and to solicit the work for competitive bidding. The program work shall be awarded to a non-profit institution with expertise in applied environmental bioremediation technology.

**Technical Point of Contact:**

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## **SERDP Thrust Area: Installation Restoration**

**Title:** Field Demonstration: Use of Hot Gas Technology to Decontaminate Excavated Underground Piping

### **Problem Statement:**

The goal of this project is to develop and implement a transportable, cost-effective, safe, and environmentally acceptable method for decontaminating excavated underground piping and sewer systems contaminated with explosives/propellants.

All DoD installations which will require clean-up of energetic contaminated areas having underground piping are targeted.

Previous pilot studies have shown that decontamination of structural components is possible using a heated gas to thermally decompose or volatilize explosives with subsequent incineration in an afterburner. To determine the feasibility of hot gas decontamination of explosives-contaminated process equipment, a pilot study was conducted at the Hawthorne Army Ammunition Plant (HWAAP) from 10 July 89 to 21 September 89. Based on results of the pilot study, test items that are treated for a minimum of 6 hours at a minimum temperature of 500 degrees F are safe for public release as scrap or in some cases, such as steel or aluminum process equipment with no intricate or mechanical components, for reuse in manufacturing or handling operations. For steel piping hot gas decon trials, no detectable contamination was found after treatment at 400 degrees F (lowest temperature evaluated in the pilot study) for 12 hours (shortest time duration evaluated at 400 degrees F). Therefore decontamination of excavated piping may be able to be performed below 400 degrees F and for shorter treatment times than 12 hours. The gas effluent from the material was treated in an afterburner system and all volatilized components were destroyed.

This program will build upon previous efforts described above. The major impetus in this program shall be to downsize the hot gas decontamination system to a size which is transportable, based upon engineering data gathered during the Hawthorne pilot study so that time and cost savings can be realized while remediating energetic contaminated federal facilities. Equipment required for this task is commercially available and none of it is proprietary in any regard. The current method of decontaminating contaminated excavated underground piping is via the manual use of a flamethrower at one end of the piping which leads to uncontrolled air emissions, is a personnel hazard, and has minimal/crude quality control associated with the decontamination effectiveness achieved. This new hot gas technology generates controlled "regulatory acceptable" emissions, reduces personnel hazards, and will have quality control/assurance program associated with it.

Clean-up of energetic contaminated piping is a significant problem in the Installation Restoration effort. At West Virginia Ordnance Works, a formerly used defense (FUD) site, seven miles of piping were recently excavated and decontaminated.

### **Project Description:**

The technical objective of this project is to conduct a field demonstration of a transportable



hot gas decontamination system which can be used to decontaminate explosive/propellant contaminated underground piping and sewer lines that have been excavated.

The Installation Restoration Data Management Information System (IRDMIS) database and other databases or information sources which characterize installation use of energetic process equipment and evidence of groundwater and soil contamination shall be reviewed to select an appropriate and representative demonstration site. This will allow potential additional field demonstration of technologies to remediate contaminated groundwater and soil located at the site and potentially share site characterization data. Site characterization shall then take place and the test plan preparation, review, and approval process can be initiated. Shortly thereafter, the safety approval and environmental permitting process can be initiated. While the safety approval and environmental permitting are being executed, site preparation and equipment assembly can commence. After all of the tasks mentioned above are completed, the field demonstration shall take place. The contaminated sewer lines and other piping will then be excavated and treated in the transportable hot gas decontamination system to verify that the down-sized transportable hot gas decontamination unit is able to decontaminate explosives contaminated process equipment, so that it can be permitted to be disposed of as scrap material. Gaseous effluent from the material will be treated in the afterburner system to destroy all volatilized contaminants.

Sufficient tests shall be conducted to verify critical parameter effects of temperature and time to assure complete decontamination. Cost savings potential will be demonstrated.

Following the test demonstration, the operating parameters of the hot gas decon system shall be optimized. Regulatory and safety compliance shall be verified. Data shall be finalized for fabrication/procurement guidance. The best deployment options shall be identified. Operating costs and savings to be realized data will be developed and reported.

Training media shall then be developed. Workshops, manuals, on the job training, and consultation, as deemed necessary and appropriate, to assist in implementation of this technology. A feedback mechanism shall then be established for determining additional research and development support which may be needed.

The approach described above will be executed through a number of tasks that include:

- 1) Site Selection
- 2) Test Plan Preparation/Review/Approval
- 3) Safety Plan Preparation/Approval
- 4) Environmental Permitting
- 5) Site Preparation/Equipment Assembly
- 6) Field Demonstration
- 7) Technology Transfer Data Package

This project is an innovative technology which permanently destroys the energetic contamination versus transferring the contamination to the air as in open burning/open detonation. This technology is transportable and will allow the treated piping to be permitted to be disposed as scrap in lieu of disposal in a hazardous waste landfill. Therefore this technology supports DoD/DOE hazardous waste minimization objectives.

The technology demonstration proposal discussed in this proposal is similar to the pilot-scale demonstration of hot gas decontamination of process buildings at Cornhusker Army Ammunition Plant (CAAP) by A.D. Little and the pilot study conducted for feasibility of a hot gas decontamination of explosives-contaminated equipment at Hawthorne Army Ammunition Plant (HWAAP) from 10 July 1989 to 21 September 1989. While similar to those efforts, however, this project will develop a scaled down version of the hot gas decontamination equipment which will minimize capital investment costs, reduce operating costs and be available for more timely clean-up of energetic contaminated facilities. Funding has been allocated for a demonstration of this technology used to decontaminate chemical agent contaminated structures. The field demonstration proposed here, to decontaminate energetic contaminated piping, is currently unfunded.

#### **Expected Payoff:**

This technology will offer a cost efficient alternative to open burning/open detonation which is currently becoming unacceptable from a regulatory standpoint and requires disposal of contaminated excavated piping and sewer lines in a hazardous waste landfill. Once the technology is accepted by the regulatory and user community it will be available for use in installation restoration or base closure activities. This technology is also applicable for explosive items, such as mines and shells, being demilitarized or scrap material contaminated with explosives. This hot gas decontamination system may also have utility for destroying military chemical agents (based upon past investigations) and other hazardous wastes which might be encountered in a remediation effort.

#### **Milestones:**

FY93: Site Selection, Test Plan Preparation/Review/Approval, Safety Plan Preparation/Approval, Environmental Permitting, Site Preparation/Equipment Assembly

FY94: Test Demonstration, Technology Transfer Data Package

#### **Transition Plan:**

Site selected and hot gas decontamination equipment selected will be those which offer the greatest potential for technical success, transition to other Federal and non-Federal sites, and possess sufficient economic advantage to encourage commercial development.

#### **Funding: (\$K)**

	<b>FY93</b>
1) Site Characterization	70
2) Test Plan Preparation/Review/Approval	100
3) Safety Plan Preparation/Approval	50
4) Environmental Permitting	50
5) Site Preparation/Equipment Assembly	400
Total	670

	<b>FY94</b>
1) Test Demonstration	300
2) Develop Technology Transfer Data Package	200
Total	500

**Performers:**

USATHAMA, DOE, and DoD installations requiring energetic contamination remediation will be the principals involved in this effort. Other agencies such as DOI and EPA may become involved if this technology proves to be effective at destroying other hazardous wastes.

**Technical Point of Contact:**

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## **SERDP Thrust Area: Installation Restoration**

**Title:** Application of the Base Catalyzed Dechlorination (BCD) Process to Dechlorination of PCB Contaminated Oil and Other Sources Found on or Associated with U.S. Navy Ships

### **Problem Statement:**

The goal of this proposal is to demonstrate the BCD process chemistry for dechlorination of PCB's found on or associated with Navy Ships, Naval Civil Engineering Laboratory, Port Hueneme, CA.

The BCD process has won the R&D 100 award in connection with the design and construction of a system for treating PCB contaminated soil in Guam. The Navy, DOE, and EPA shared this award. The process operates at temperatures up to 350°C and uses a variety of common alkaline chemicals in combination with other inexpensive materials. It has been shown capable of dechlorinating to very low levels soils, contaminated oils and contaminated debris from transformers. The process should be readily applicable to contaminated materials and debris associated with navel vessels and operations.

New program or enhancement or previously funded effort - Although this work was not funded previously under this program, as indicated in the background discussion, related studies were funded by both EPA and the Navy.

### **Project Description:**

The objective is to demonstrate an efficient cost effective means of remediation of PCB contaminated materials associated with navel vessels. For those materials that can be physically removed, an appropriate chemical treatment system would be designed, constructed and operated to demonstrate dechlorination. Where removal of contaminated materials to a reactor is not possible, an extraction process would be developed to operate in conjunction with the chemical treatment system.

Laboratory scale tests would be performed to define the chemical dose and operating conditions for each waste including those extracted from contaminated materials that cannot be directly treated. A reactor would be designed and constructed for carrying out field scale runs. One or more extraction procedures might have to be devised for the materials that cannot be directly treated.

Both DoD and DOE have similar problems of PCB mixed waste and PCB contaminated materials. Thus the DoD application of BCD if successful could enhance the DOE efforts to solve their problems. This application is an extension of work which led to the development of a system for treating soil in Guam. Other units have been used to treat contaminated soil and contaminated oils.

The initiation of this project at a laboratory level will minimize any risk Demonstration of the BCD process at full scale on soil and pilot studies with other wastes indicate the possibility of technical risks is very small.

**Expected Payoff:**

More than four years of experience with BCD chemistry treating soils and other solid and liquid wastes indicates direct applicability to treatment of oils and debris. The benefit would be an economical, non thermal method of remediation. As already indicated, the capability of the BCD processes has been demonstrated. the cost of the process depends strongly upon the type of waste, but for soil treatment has been estimated to be cheaper than any other method. For treatment of contaminated oil, a number of companies have selected this process for commercial use in foreign countries.

**Milestones:**

It is expected that the process would first be tested on the various PCB contaminated materials at the laboratory level. Required time would be six to nine months for directly treated wastes. For contaminants to be extracted, extraction procedures would be developed over this time period and the extracts treated toward the end of the laboratory tests. A small demonstration reactor, several hundred gallons, would be constructed. Completion should be 18 months after project initiation. Operation would require an additional year.

**Transition Plan:**

The demonstration reactor should have immediate use for treatment of some wastes. Larger reactors could be designed easily from the demonstration unit. Ability for the private sector to assure production of necessary equipment should be simple. Close coordination between EPA and the Navy is expected as was experienced during design of the Guam treatment system. Final report would facilitate broad use.

**Funding: (\$K)**

	<b>FY93</b>	<b>Total</b>
Laboratory studies and design of reactor	150	400
Extraction studies	100	
Initiation of reactor construction	150	
	<b>FY94</b>	<b>Total</b>
Completion of reactor	100	300
Demonstration of reactor	200	

**Performers:**

RREL; NCEL.

**Technical Point of Contact:**

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## Pollution Prevention

Project Title	Page Number	Funding FY93 (K)
Metal Working Processes		
Non-Chemical Surface Preparation (AF)	350	300
Electro Magnetic Powder Spray (AF)	354	300
Laser Cleaning and Coatings Removal (AF)	358	350
Waterjet Paint Stripping (A)	362	450
PVD Coatings and Ion Beam Processing as Alternatives to Electroplating (A)	364	485
Recovery/Recycling/Purification of Plating/Cleaning Baths (N)	370	600
Solid State Metal Cleaning (AF)	373	350
Noncyanide Strippers to Replace Cyanide Strippers (AF)	377	1,100
Alternative Process to Acid Cleaning/Degreasing of Depleted Uranium (A)	379	125
Nonchromatic/Noncarcinogenic Etching for Bonded Structures (A)	381	350
Electroplating Waste Reduction (N)	383	460
In-Tank Treatment of Acid and Alkaline Cleaners (A)	386	250
Alternative Paint Stripper for Powder and Electrodeposition Coatings (A)	388	190
Environmentally Acceptable Heat Treating (A)	389	265
Pre-Paint Non-ODC Batch Cleaning (A)	391	150
Investigation of Aqueous Cleaning Systems (A)	394	120
Cadmium Plating Alternatives (A)	396	270
Coatings and Applications		
Aircraft Maintenance Chromium Replacement (N)	397	170
Nonchromate Conversion Coatings for Aluminum Alloys (A)	400	245
Accelerated Testing Techniques for Environmentally Acceptable Materials and Processes (AF)	403	100

Project Title	Page Number	Funding FY93 (K)
Non-Hazardous, Low VOC Corrosion Protection Paints and Coatings (N)	407	3,500
Innovative Very Low VOC Antifouling Paints and Processes (N)	410	570
Large Area Powder Coating (AF)	413	100
Organic Protective Coatings and Application Technology (N)	417	490
Investigate Water-Based Coating Systems for Military Clothing and Equipment (A)	420	130
Nonvolatile Organic Compound Chemical Agent Resistant Coating (A)	422	150
Flame Spray of Thermal Plastic Coatings (A)	424	100
Ordnance Processing		
Joint DoD/DOE Program for Agile, Clean Manufacturing Technology for Propellants, Explosives, and Pyrotechnics (DoD/DOE)	425	2,000
Development of Non-Polluting Primary Explosives (A)	430	267
Plutonium and Uranium Metal Forming Technologies (DOE)	432	5,000
Electron Beam Melting and In-Process Scrap Recycling of Uranium (DOE)	438	1,300
Continuous Oxide Reduction System (DOE)	444	371
Application of Supercritical Fluid Extraction and Supercritical Chromatography to Analysis of Energetic Materials (A)	448	200
Depleted Uranium Waste Minimization and Material Reutilization (A)	450	350
Ozone Depleting Substances Replacement		
High Efficiency Magnetic Bearing Lubrication-free Centrifugal Compressor for Use with Environmentally Safe Alternate Refrigerants (AF)	452	250
Research in CFC Substitutes (A)	455	100
Encapsulated Micron Aerosol Agent Technology (AF)	457	650
Chemical and Physical Processes Responsible for Flame Inhibition Using Halon Agents and Their Alternatives (A)	460	300

Project Title	Page Number	Funding FY93 (K)
VOC and Hazardous Air Pollutant Emissions Reduction for Painting, Cleaning and Vapor Degreasing Facilities (EPA)	463	2,750
Alternatives to Halon 1301 for Ground Vehicle Compartments (A)	468	1,524
Evaluate Replacements for ODSs Used in Military Related Refrigeration Systems (EPA)	470	300
Hazardous Waste Reduction, In-Process Recycling or Elimination		
Propellant Recycling (N)	473	100
Elimination of Lead and Antimony Compounds in Solid Film Lubricants (A)	476	100
An Environmental Knowledge Based Advisor for Facilities Life Cycle Decisions (EPA)	478	500
Alternate Solvents for Propellant Manufacture (A)	482	210
Solventless Pyrotechnic Manufacturing (N)	484	355
Extraction and Recycling of LOVA Propellants Using Supercritical Fluids (A)	489	400
Heavy Metal Discharge from Ship Ballast (N)	492	225
Evaluating Clean Technology Implementation (EPA)	494	500
Packaging		
Verification of Shelf-life for Hazardous Materials (N)	497	200
Hazardous Materials Substitutes		
Advance Nickel-Metal Hydride Battery (AF)	499	300
Solvent Substitution and Low VOC Cleaners (N)	501	170
Non-Emulsifying Degreasers for Shipboard Use (N)	504	190
Minimization of Solvents used in Analyzing Mixed or Hazardous Wastes (DOE)	506	360
Data Bases		
Expanding the Pollution Prevention Information Exchange System (PIES) to Serve as a Communication and PP Network of Technical Information for Other Federal Agencies (EPA)	511	900



Project Title	Page Number	Funding FY93 (K)
Reduce Greenhouse Gas Emissions		
Contribution of Mixing to Formation of Nox in Gas Turbine Compressors (AF)	516	240
Total		31,782

## **SERDP Thrust Area: Pollution Prevention**

### **Title: Non-Chemical Surface Preparation**

#### **Problem Statement:**

Conventional cleaning and surface treatment processes used in the aerospace industry often involve use of toxic materials and solvents and generation of aqueous hazardous waste streams. These processes involve toxic hazards in the workplace, risk of uncontrolled releases of hazardous substances, and treatment and disposal procedures which are costly, administratively burdensome, and attended by serious legal and financial liabilities. In addition, many traditional materials, such as ozone depleting chemicals, are subject to bans on production and use.

The goal is to develop surface preparations for aluminum and titanium alloys that eliminate or minimize use of hazardous materials such as hexavalent chromium, strong oxidizing acids or concentrated bases or generation of large amounts of contaminated wastewater.

State of the art surface treatments for aluminum and titanium alloys generate large amounts of wastewater within the process and/or incident to waste treatment. Treatment processes themselves require the use and handling of hazardous acids and bases. Further, the increased emphasis on reduction of volatile organic compound (VOC) and air toxics emissions will dramatically increase the wastewater stream from surface preparation processes. Management, treatment, and disposal of these hazardous materials and wastes are increasingly costly, burdensome, and constantly attended by the risk of enforcement actions by local, state, and federal authorities. The development of metal surface preparations that do not require use or generation of hazardous substances will significantly aid the Air Force in meeting its pollution prevention goals. This is a new project for FY93 SERDP.

#### **Project Description:**

The objective is to identify, develop, and optimize non-wet chemistry approaches for the formation of stable morphologies on the surface of aluminum, titanium and copper materials that will allow performance of high quality coating or adhesive bonding.

This program will involve laboratory R&D, process scale-up, specifications development, and technology transition in two specific technical areas. These areas are (1) laser surface preparation of aluminum and titanium alloys. The feasibility of the use of the excimer laser to grow oxides on aluminum has been shown, and the bondability to both coatings and adhesives has been demonstrated. (2) non-chemical surface morphologies for coating and bonding to aluminum, titanium, and copper can be achieved via non-chemistry based processes including plasma spray, flame spray, and vapor deposition. These approaches are based on new technology and initial feasibility has been demonstrated. Processes currently in use are based on wet chemistry and require use of soluble chromate, strong acids and bases and large amounts of water. The use and generation of toxics is an increasingly risky and expensive proposition. The new approaches represent a radical, but environmentally benign, departure from existing technology. There are no serious technological roadblocks foreseen in the scale-up of these processes.

Previous efforts/accomplishments in this area within and outside the organization: This technical effort will build on recent efforts in cooperation with EOARD to develop CO<sub>2</sub> laser surface modification technology.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort will also enable reduction of risks, costs and liabilities associated with use of toxics, and handling, treatment and disposal of hazardous wastes. In some instances, elimination of ozone depleting chemicals (ODCs) may be achieved. This project will support the Air Force goal to reduce hazardous waste generation by 50% by the end of 1999 (1992 baseline).

Related activities include work on solid state cleaning of metals and thin film deposition technology, the AF Civil Engineering Support Activity (AFCESA) spray casting program and thin film (including sol gel) deposition technology developed for the electronic and commercial construction industry.

#### Tasks/activities:

Experiments will be conducted to determine the feasibility of developing surface oxide morphologies that are thermodynamically stable, mechanically strong, and resistant to corrosion (chemically stable).

Technology areas to be investigated will include sol gel films, thin film deposition of SiC, SiN, SiO, sputtered and enhanced ion-beam deposition coatings as well as laser enhanced oxide formation.

Additional tasks include: 1) Surface laser characterization will be accomplished using various surface analysis techniques. 2) Chemical and thermodynamic stability of coatings will be determined. 3) Corrosion resistance and performance of coatings and adhesive bonded joints will be studied. 4) Bench top process equipment will be developed and process parameters optimized. 5) Testing and analysis will continue and life cycle cost studies will be performed. 6) Scale up to pilot size equipment will be accomplished. 7) Specifications and standards will be written. 8) Processes will be optimized.

Pilot scale equipment will be operated so that users may have short production runs performed on components prior to more extensive field service applications.

Technical issues to overcome: The technical risks include the ability to produce the desired oxide morphology with the requisite thermodynamic and chemical stability and the needed mechanical strength without degrading the substrate mechanical properties. Attending these risks are the challenges of developing technology that will be environmentally acceptable and affordable.

#### Expected Payoff:

Potential users - government/public: Breakthrough technologies to prepare metal surfaces in various stages of manufacturing and remanufacturing will be of enormous benefit to aerospace and other industries in the US and worldwide. The total cost avoidance will be

dependent upon the specific applications and the technologies developed. While direct labor, material, and equipment costs may increase, they may be offset by eliminating the costs of hazardous materials and waste management and environmental compliance and response.

Impact - It has been demonstrated that environmentally benign alternative materials and processes can be less costly, more effective, and less time consuming than the technology replaced. Although there is a risk of adverse cost, performance, or schedule impact, the technical effort will endeavor to eliminate or minimize any such impact.

#### **Milestones:**

FY93:

JUL - Project go-ahead

AUG - Initiate laboratory development and tests of candidate materials and processes.

- Define processes to be replaced and applicable specifications and standards.
- Define process mechanisms and critical process parameters.

SEP - Select candidate processes for more extensive testing.

FY94:

DEC - Select most promising materials and processes for more extensive testing.

MAR - Initiate large laboratory scale process studies. Initiate process parameter sensitivity studies.

JUN - Initiate studies on surface stability and strength.

- Initiate coating and bonding studies.

SEP - Complete all preliminary tests and studies. Initiate scale-up to pilot scale process facility.

FY95:

DEC - Initiate optimization of pilot scale process.

- Begin treatment of customer furnished components for extended service evaluation.
- Prepare or revise specifications and standards.

**Funding: (\$K)**

FY93	FY94
300	950

**Transition Plan:**

The proposed R&D program will be accomplished in an integrated program development mode. The pilot plant will be operated at the Developmental Manufacturing and Modification Facility (DMMF) at Wright-Patterson AFB, OH or at one of the Air Logistics Centers in cooperation with a user team. Successful service experience along with specifications and standards will enable each prospective user to implement processes meeting their specific needs. Potential users will be an integral part of the R&D team to ensure that their inputs will be incorporated on a continuous basis into the technology development cycle.

**Performers:**

The project will be performed under the technical leadership and direction of the following:

Air Force Materiel Command  
Aeronautical Systems Center  
Wright Laboratory  
Materials Directorate (WL\ML)  
Wright-Patterson AFB, OH 45433

The Materials Directorate will award one or more research contracts to industry to perform the development and integration.

**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

**Title:** Electro Magnetic Powder Spray

### **Problem Statement:**

The goal of this program is to develop environmentally benign materials and processes to deposit or remove chromium, nickel, or copper on metal parts.

New technology is needed as an alternative to traditional electroplating and plating removal methods which depend heavily on use of hazardous and toxic materials and generate volumes of hazardous wastes which must be managed, treated and disposed of. A number of alternative technologies are being pursued within the government and the private sector which eliminate the need for toxic use and generation. Many of these involve flame or plasma deposition. Wright Laboratory has participated in many of these development efforts. Review of research sponsored or performed by the Department of Energy and other researchers has generated interest by Wright Laboratory in a potential "leapfrog" technology based on very high energy deposition using a rail gun concept. The potential exists for using pulsed power sources for high density powder consolidation and deposition on a variety of substrates. Railgun technologies have a major advantage over other accelerator technologies in that the acceleration of the models can be kept under complete control throughout the acceleration process. Experimental results to date suggest that high-energy high-rate processing in this manner promises a novel, environmentally benign means of metal surface modification. This is a new project for FY93 SERDP.

### **Project Description:**

The objective of the planned effort is to develop and introduce new technology to deposit and strip coatings of copper, nickel, and chromium from metal parts, especially aircraft engine parts, such as shafts, gears and vanes.

The proposed project will involve research and development in use of hypersonic energy techniques to (1) deposit material on selected aerospace parts and (2) remove material deposited by such techniques. Study will be conducted of the physical and chemical basis for this potential breakthrough technology. Considerations in identifying an acceptable technology will include: maintenance or improvement of product quality and performance in connection with both deposition and removal; effects of part geometries on process effectiveness (especially thickness); process reliability and quality assurance, and environmental health and safety. Research findings associated with the rail gun concept will be assembled and evaluated. Development needs will be identified and implemented. An optimum technical approach will be developed, scaled up, demonstrated and qualified. As previously stated, needs of Air Logistics Centers (ALCs) and Government-Owned, Contractor-Operated (GOCO) facilities will be given priority attention.

Research on the subject of rail gun technologies has been performed by AF Aero-Propulsion Laboratory, US Department of Energy, University of Texas, Aberdeen Proving Grounds and others. No other government or industry sponsored work is known to be ongoing or

planned dealing with hypervelocity deposition of copper, nickel, and chromium for industrial applications.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort will also enable reduction of risks, compliance costs and liabilities associated with use and release of toxics to the environment associated with traditional electroplating processes.

Planned efforts on solid state cleaning will feed into the overall processes to be developed by this effort. Wright Laboratory EOARD work with Technion in Israel and investigation of thin film deposition technologies are also relevant. AF Civil Engineering Support Activity (AFCESA) spray casting development efforts also bear on the proposed effort.

Process studies will be conducted to identify and assess candidate technologies for both deposition and removal. Studies of development needs will be identified and implemented. The most promising technology alternatives will be selected for testing, analysis, development, optimization, scale up, demonstration and qualification. Life cycle cost studies will be performed which will include production cost estimates. Prototype will be transitioned to users for extended production evaluation. Needs of Air Logistics Centers (ALCs) and Government-Owned, Contractor-Operated (GOCO) facilities will be given priority attention.

New technology must be developed that is environmentally acceptable and affordable and able to compete with technologies that have been used and optimized over more than 40 years. The concept is innovative and the risks are high, but the potential payoff justifies the investment. The principal technical issue is to develop optimum parameters for material condition, impact velocity, current waveshape, target condition and distance, target temperature, and chamber atmospheric conditions.

#### **Expected Payoff:**

Potential users - government/public: Availability of usable non-electroplate deposition\removal processes to the aerospace industry will free Air Force and industry users from the burdens of using a technology dependent on chromates and cyanides. The total cost avoidance will be dependent upon the specific applications and the technologies developed. While direct labor, material, and equipment costs may increase, the burdens of environmental compliance and costs of hazardous materials and waste management and response will be entirely eliminated.

Impact: The planned effort will be redirected or terminated if it involves unavoidable adverse impact to weapon system efficiency, capability, or schedule. If successful, the effort will provide a cost effective and environmentally safe alternative to use of toxic materials and processes.

**Milestones:**

FY 93

JUL: a) Initiate project. b) Initiate studies to define deposition process physical and mechanical characteristics, to define critical process parameters for both deposition and removal, and determine materials properties.

SEP: a) Complete definition studies. b) Initiate selection of parts and processes to be targeted for development and application of the new technology. c) Initiate preparation of experimental design for initial technology demonstration.

FY 94

NOV: a) Finalize deposition technology demonstration agenda. b) Select site for deposition demonstration. c) Initiate preparations for technology demonstration.

MAR: a) Conduct deposition technology demonstration. b) Initiate analysis of results in concert with research partners and user technical representatives.

SEP: a) Initiate studies of removal process options. b) Design and initiate tests and experiments to address removal effectiveness and effects on integrity of coated parts.

FY 95

NOV: Initiate validation studies for both deposition and removal processes to address materials performance and integrity, process quality and consistency, and system performance validation.

MAR: Complete validation studies. Determine if scale up studies are warranted. If so, develop and initiate a pilot scale demonstration plan aimed at determining full scale process requirements and characteristics.

APR: Complete pilot scale demonstration plan. Initiate actions to perform pilot scale demonstration.

SEP: Complete pilot scale demonstration. Review results with users and research partners and determine whether full scale demonstration is warranted.

**Funding: (\$K)**

FY93	FY94
300	600



**Transition Plan:**

Following decision to perform full scale demonstration, a demonstration plan will be developed in concert with the user for the selected demonstration site (Air Logistics Center or DMMF at Wright Patterson AFB OH). Performance testing parameters will be developed, equipment and materials procured and positioned, and staffing and support arranged. Full scale demonstration will then be conducted. Findings will then be compiled and made available to prospective users for review and evaluation. After evaluation and acceptance, specifications and standards will be prepared or revised to make the new technology available for production or logistics use.

Potential users will be an integral part of the R&D effort for its duration. Their participation and technical inputs will be utilized throughout the technology development and validation process.

**Performers:**

The project will be performed under the technical leadership and direction of the following:

Air Force Materiel Command  
Aeronautical Systems Center  
Wright Laboratory  
Materials Directorate  
Wright-Patterson AFB, OH 45433

The Materials Directorate will award one or more research contracts to industry to perform the development and integration.

In order to facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans on having the demonstration site to be either an Air Force Materiel Command Air Logistics Center or the Developmental Manufacturing and Modification Facility (DMMF) at Wright-Patterson AFB Ohio.

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Laser Cleaning and Coatings Removal**

#### **Problem Statement:**

New, automated aircraft paint removal systems are currently being developed to depaint or strip aircraft metallic and composite structures. However, these systems do not have the capability to efficiently and safely remove paint and other coatings from aircraft radomes and other components. Aircraft radomes must conform to stringent performance criteria to ensure accurate initial launch coordinates for missiles, artillery, and safe terrain avoidance/mapping information. Depot radome repairs consists of removing or "stripping" multi-layer dielectric coatings, filling and smoothing voids in the radome wall, and then applying new dielectric coatings onto the radome surface. Currently, there are four different coating systems that are applied to the radomes. These coating systems must be removed for depot inspection and repair. Today, the coatings are manually removed using hazardous chemicals which expose workers to potentially unsafe practices. The stripping procedure is performed in a paint booth with personnel using air supplied respirators. Workers must also wear protective equipment such as goggles, gloves and coveralls. During the stripping of the radome dielectric coatings, solvents are released to the atmosphere and toxic hazardous waste (contaminated paint residue and rags) is generated creating disposal problems. These practices must be discontinued as soon as possible to achieve DoD and Air Force Pollution Prevention goals. An automated system using laser, or other stripping technologies is required to remove personnel from this hazardous process and conform to local, state, and federal pollution prevention laws.

The goal of the proposed effort is to provide a field demonstration of a prototype laser-based facility to demonstrate environmentally acceptable component cleaning and coating removal technology and to transition it to the Air Force Logistic Centers and other aerospace users.

Targeted departments and organizations include Oklahoma City Air Logistics Center (OC-ALC), San Antonio Air Logistics Center (SA-ALC), Warner Robbins Air Logistics Center (WR-ALC), Sacramento Air Logistics Center (SM-ALC), and Ogden Air Logistics Center (OO-ALC).

Cleaning and coatings removal technologies have traditionally depended upon the use of organic solutions, such as, PD 680 (I, II, & III) methyl ethyl ketone (MEK), methylene chloride (MECL), phenol, and strong acids and bases, as well as hot potassium permanganate solutions. These materials are hazardous, and include volatile organic compounds (VOCs), ozone depleting chemicals (ODCs) and air toxic emitters which are subject to severe restrictions or are being banned altogether, such as freon (CFC-113). More recently, the trend in cleaning technology is toward the use of water-based cleaners (sodium metasilicate, bases, terpene/water emulsions or water detergent blends), some of which may be hazardous to some degree. However, technologies are needed which do not involve generation of waste water streams.

This is a new program. Laser-based cleaning and coating removal has been demonstrated to be an environmentally acceptable, affordable and controllable technology. A demonstration

facility is needed to facilitate transition of this technology to Air Force, DoD and industry use, targeted to the immediate needs of the Air Logistics Centers.

#### **Project Description:**

The project objective is to demonstrate the use of laser cleaning and coating removal on components ranging from turbine engine blades to landing gear and radomes.

The project approach is to design, fabricate test, evaluate and demonstrate a state-of-the-art automated, controllable laser cleaning and coating removal facility. The facility will be designed for carbon dioxide and eximer laser cleaning and coating removal operations. System operation will be fully robotized and computer controlled with on-line instrumentation for component positioning and measuring and controlling laser inputs to the part surfaces.

Tasks associated with this project include:

a) Design system to demonstrate technology on fighter aircraft landing gear and radome components. b) Design a subsystem system to handle, treat or capture, as necessary, all gaseous and particulate products of the process. c) Purchase or fabricate lasers, computers, robotics, controller, sensors, hardware and software necessary for the operation of the system. d) Assemble the demonstration facility system. Make necessary mechanical hardware and software modifications to insure safe, reliable and controllable operations. e) Demonstrate system on both metallic and non-metallic specimens. f) Test and evaluate adequacy of cleaning and coating removal process for aircraft components. g) Operate the facility and make it available for ALC and GOCO engineering evaluation on specific aircraft components. Qualify facility to applicable specifications for aircraft components cleaning and coating removal.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort also will enable reduction of risks, compliance costs and liabilities associated with use and release of toxics to the environment. This program supports the DoD objectives to reduce volatile air emissions by 50% by the end of 1999 (1993 baseline).

Extensive test and evaluation work has been completed by the Air Force and the Navy on laser radiation effects on substrate materials and coating removals. What is needed next is a prototype facility where test and evaluation cost analysis and cleanliness levels can be performed on a variety of aircraft components. The facility would be available to the services as well as the aerospace community for test and evaluation purposes.

The technical risks involved in this project are low. Industrial lasers, both carbon dioxide and eximer are available; controls, robotics sensors, instrumentation are also available. Software will have to be developed/modified to control the production system. Systems design must incorporate all applicable safety devices and features.

### Expected Payoff:

The laser-based cleaning and coating removal facility will be applicable to a broad range of aircraft and general equipment cleaning and coatings removal work. Benefits include the complete elimination of the use of toxics and hazardous waste generation in logistic center maintenance and re-manufacturing operations relying on the new technology. The limits of such potential payoffs are presently unexplored and remain to be determined. The process is expected to be highly cost effective considering that all costs for hazardous materials management and management of solid, liquid, and vapor waste streams will be eliminated.

### Milestones:

	FY93
Project Initiation/start	Jul
Initiate preliminary systems requirements study	
Complete preliminary systems requirements study	Sep
	FY94
Complete detailed systems analysis design	Dec
Initiate design review process	
Approve Design	Mar
Initiate hardware procurement/component fabrication	
Initiate life cycle cost study	May
Initiate systems assembly and check-out operations	Aug
	FY95
Complete life cycle cost studies and economic benefit studies	Aug
Final report and transfer of system to selected ALC	Sep
Complete check-out and de-bug of system operations	Oct
Initiate test and evaluation with services and industry customers	Dec

### Transition Plan:

It is planned that the system to be built under this effort will be a prototype demonstration and as such will have many more capabilities than required on an actual production system. Users will perform test and evaluation programs on the prototype and determine the capabilities needed for their production unit. Cost data will be generated, specific engineering problems will be addressed and production systems design requirements will be generated.

### Funding: (\$K)

FY93	FY94
350	2000

**Performers:**

The project will be performed under the technical leadership and direction of the following:

Air Force Materiel Command  
Aeronautical Systems Center  
Wright Laboratory  
Materials Directorate  
Wright-Patterson AFB, OH 45433

The Materials Directorate will award one or more research contracts to industry to perform the development and integration.

In order to facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans on having the demonstration site to be either an Air Force Materiel Command Air Logistics Center or the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB Ohio.

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## **SERDP Thrust Area: Pollution Prevention**

**Title:** Waterjet Paint Stripping

### **Problem Statement:**

Traditional paint stripping processes involve hazardous wet chemicals and abrasives such as sand, steel shot, and plastic media. All of the above produce large amounts of hazardous waste. The objective is to develop a methodology to eliminate these hazardous wastes. A candidate methodology is waterjet stripping, which eliminates 95 percent of the problem with waste and disposal.

### **Project Description:**

The program objective is to develop a waterjet system that would eliminate or greatly reduce hazardous wastes that are currently produced when wet chemicals, or abrasives, are used to remove paint from military hardware. Proof of waterjet principle of paint stripping was completed in FY 92 at United Technologies, Inc. (6.3A). The development of software programs for robotic application would be conducted, as well as characterizing requirements for each weapon system, and installing the system at the pilot plant facility at FMC Corporation.

### **Expected Payoff:**

The military items benefitted by this system would include: the M113, BVFS, M915, M1A1, HUMMWV, various munitions, and all rebuild programs currently in progress at depots. The waterjet system would eliminate costly disposal of hazardous waste. Currently the cost of removal of hazardous waste is estimated at \$500-600 per barrel. Additionally, the system would eliminate undue exposure of hazardous dust to personnel and potential explosive hazards.

### **Milestones:**

Characterize each selected weapon system needs	1Q FY94
Develop appropriate software package for robotics	3Q FY94
Do a pilot run at contractor site FMC Corporation	4Q FY94
Test and write final report	1Q FY95
Full production	2Q FY95

### **Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
SERDP	450	300
In-House (6.3A)	40	40

### **Performers:**

United Technologies, FMC Corporation, and Cape Cod Research.

**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: PVD Coatings and Ion Beam Processing as an Alternative to Electroplating**

#### **Problem Statement:**

The goal of this project is to conduct applied research and development to demonstrate that metal or ceramic coatings deposited by; physical vapor deposition (PVD), and/or ion-beam-modified surfaces are equivalent or superior in performance and are a cost-effective alternative to electroplated chromium and cadmium.

Hard chrome is primarily used in DoD-related manufacturing to coat high-wear surfaces such as bearing shafts and hydraulic components and is principally performed by Original Equipment Manufacturers and to rebuild and remanufacture out-of-tolerance components, such as worn shafts and corroded hydraulic components, with the work being performed by maintenance depots. For the former, the use of hard chrome has actually been increasing because the general requirement for coatings has also been increasing due to enhanced performance requirements. For example, GE Aircraft Engines currently applies hard chrome to 1192 different engine components. For the latter application, many pieces of military hardware are returned to the depots for refurbishment with components that are worn, corroded, or eroded by use. Rather than replacing them, they are reworked by removing the damaged metal, stripping off any old hard-chromium coatings, building them up with hard-chrome, and then matching them to final tolerance. As an example of usage, at the Corpus Christi Army Depot, where most of the Army's helicopters are serviced, annually more than 10,000 separate types of components are coated with hard-chrome for this purpose. It should be noted that most of these components are reworked and re-plated several times. To provide an indication of costs associated with chrome plating, it is estimated that for each plating line the cost of waste disposal is \$10,000 per month with the total cost associated with installation of a new plating shop that meets EPA and OSHA regulations ranging from \$5M to \$15M.

Gun tube wear and erosion have been a long-standing Army problem. A practical objective has been to achieve gun tube wear life comparable to fatigue life. The unexpectedly short tube life for the new 8" and 155 mm gun systems was revealed by wear and erosion tests late in the development cycle. Further, the Army has a strong interest in pushing towards higher gun performance to extend the range of its artillery and to obtain higher velocities and shorter times of flight for rapid-fire anti-aircraft guns. The problem remains to obtain acceptable tube life with higher performance. Modern high performance guns require erosion protection. Chromium plating of gun tubes has provided a finite improvement in tube life depending on gun operating conditions. But the mechanical stability of CR electroplate (due to numerous microcracks) is limited and new protective coatings with even higher melting points (refractory metals) are needed to challenge the use of more energetic propellants which have higher flame temperatures. Reduction in the use of electroplated chromium will result in an appreciable reduction of the Army's cost of safe handling and disposal of hazardous waste (estimate to be greater than \$335M in 1991).

Cadmium electroplating is also used by both OEM's and by DoD maintenance depots to impart corrosion resistance and lubricity to a wide variety of parts, although substitute



coating processes have been more fully developed for this than for the hard-chrome plating. These alternatives include electrodeposited Zn alloys and ion-vapor-deposited (IVD) aluminum. The Air Force has taken the lead in the actual implementation of these alternatives. At other facilities, such as the Cherry Point Naval Aviation Depot, which has had an IVD system for almost 10 years, the ratio of Cd-plated to IVD-coated parts is more than 10 to 1. The Anniston Army Dept, Anniston, Alabama, has recently installed two IVD systems and is replacing cadmium with IVD aluminum for certain components of armored vehicles other than fasteners. The Air Force acknowledges that IVD-Al will not replace more than about 50% of the Cd-plating requirements. The Army has authorized electroplated zinc as an alternative to cadmium for grade 8 fastener applications. Concurrence by the Air Force and Navy to accept zinc as a legitimate alternative to cadmium for the fasteners has also been obtained. Exceptions include selected electrical or electronic applications where cadmium-plated fasteners are required or preferred and high-strength steels for certain helicopter components. A recent preliminary laboratory study by the Army Research Laboratory, Watertown Site, showed a Zn-Ni alloy provided better corrosion resistance than zinc and exhibited a comparable coefficient of friction. Thus there still exists the strong need for further coating development efforts.

### **Project Description:**

Most previous efforts in this area have been the investigation of alternative electroplated coatings, such as Zn alloys to replace cadmium. The only significant exception to this is the development of IVD aluminum. It is interesting to note that large-scale IVD-Al systems have been available for over 15 years, yet DoD is still funding R&D work to investigate this process. Electroless nickel coatings are also being investigated as a replacement for chrome, but nickel is on the EPA "toxic enemies" list, so it should only be considered as an interim replacement process.

The technical objective is to demonstrate PVD coating techniques and ion beam processing as effective environmentally acceptable alternatives to chromium electroplating. Vacuum-based PVD coating techniques are known to produce the highest quality coatings, with widespread use of high vacuum techniques in the microelectronics industry having broadened the industrial base for large scale systems with a concomitant reduction in cost. The most advanced types of PVD coating techniques utilize what can be called "ion-assist", whereby energetic charged particles are incident on the workpiece during the coating process. Two variations on the ion-assisted PVD are ion-beam-assisted deposition (IABD), whereby a directed beam of energetic particles from an ion gun are coincident on the workpiece with the depositing vapor atoms and magnetron sputtering, whereby vapor atoms are produced by sputtering from an electrode with ions being accelerated from a plasma by application of a negative bias to the workpiece. These two techniques produce coatings that are highly adherent, fine grained, generally pin-hole free and fully dense, and which can be deposited at relatively low temperatures on virtually any type of solid material. The deposition rates for these types of coating techniques are sufficiently high that they could be expected to economically replace both chrome platings deposited by OEM's and electroplated cadmium. For these applications, the types of coatings to be investigated would be TiN, (Ti,Al)N, CrN, Ta, and diamond-like carbon, all of which have been previously investigated for corrosion and wear applications. However, the deposition rates are not high enough to replace the chrome plating operations in military depots which are intended for re-build of components.

For this application, the proposed solution is to rebuild the component using an alternative electroplating technique, such as electroless nickel, machine it to final tolerance, and then apply one of the above PVD coatings which should provide significant wear and corrosion resistance, leading to a reduced requirement for future rework.

Ion implantation has been shown to significantly improve the corrosion and wear behavior of a variety of materials. With this technique, near-surface alloys or compounds can be produced, with no discrete interface between the modified layer and underlying material that could lead to delamination problems as is possible with coatings. Virtually any element can be implanted into substrate materials, although only a few will be selected for this program. Previous research conducted at ARL has shown that nitrogen implantation into hard-chrome coatings increases the surface hardness and significantly reduces the tendency of the coatings to form microcracks when subjected to loads or stresses. This will be further investigated under this program as well as ion implantation of thin-dense-chrome coatings, a proprietary process of Armoloy, Inc., which is an electroplating process that does not produce toxic effluents.

This proposal addresses the DoD environmental objectives of eliminating airborne toxic emissions and hazardous waste streams associated with chromium and cadmium electroplating. The treatment of these hazardous effluents at the many installations utilizing these processes is estimated to cost DoD tens of millions of dollars each year.

Relationship to other similar ongoing work: In November 1992, the Basic Industry Research Laboratory (BIRL) at Northwestern University was notified by DARPA that they will be awarded a substantial contract (\$1.5M over two years) entitled, "Hard-Chrome Coatings: Advanced Technology for Waste Elimination." A major portion of this contract will be to investigate methods for reclaiming or recycling effluents from the plating operations. Another significant portion is the investigation of alternative coating processes. These include HVOF plasma spraying, laser cladding, laser-assisted chemical vapor deposition, and sputtering. The Surface Modification Branch at NRL will have a small effort under the DARPA program (\$30K per year) to perform ion-beam modification of some of the coatings. This proposed SERDP program is designed to investigate other coating techniques and thus there would be virtually no duplication of effort. One of the POC's (BDS) on this proposal has previously collaborated with the PI on the DARPA contract in other areas and it is anticipated that there would be extensive sharing of results between the two programs to ensure that DoD would obtain optimum solution(s) to this problem.

Since it will not be necessary to demonstrate that the coating techniques to be investigated under this program are environmentally acceptable, the focus of the project will be the characterization and evaluation of the coatings in comparison to electroplated chromium and cadmium coatings. Evaluation of coating performance must include laboratory simulation of the conditions to which coated components will be subjected and baseline comparison with hard-chrome-coated components. Properties such as hardness, adhesion, and density will be determined for all the coatings. Measurements related to actual performance will be correlated with the type of electroplated coating intended to be replaced and the actual end-use application. Thus, appropriate tests could include sliding wear tests with realistic loads, speeds, and use of lubricants; erosion tests; corrosion test using electrochemical and/or salt spray methods; low-cycle or high-cycle fatigue, or rolling-contact fatigue. In addition to

evaluation of coated test coupons, actual components will be selected for coating and evaluation in rig tests at appropriate depots. The POC's have assembled a team that can address all of the tasks related to coating deposition, characterization, and evaluation.

#### **Tasks and Activities:**

Deposition of IABD and plasma-sprayed coatings; cohesion, adhesion, and porosity measurements on all coatings; surface analytical measurements; corrosion by electrochemical impedance spectroscopy, galvanic corrosion studies; erosion tests; coefficient of friction measurements; rolling contact fatigue measurements-Corrosion Science Group, ARL.

Deposition of IBAD coatings; hardness, density, and adhesion measurements on all coatings; composition measurements on compound coatings and determination of impurities, if any; other surface analytical measurements; sliding wear tests; electrochemical corrosion tests-Surface Modification Branch, NRL.

Deposition of magnetron sputtered coatings; high-temperature wear test using Palex tester-BIRL, Northwestern University.

Deposition of PVD coatings-Jet Process Corporation, New Haven, CT.

Deposition of TDC coatings-Armoloy of Connecticut, Inc.

Fatigue testing of coated samples-Naval Air Warfare Center, Trenton, NJ.

Deposition of cadmium and chromium coatings onto test specimens; selection of two helicopter engine or transmission components (in consultation with ARL) for coating; rig testing of coated components-Corpus Christi Army Depot (CCAD).

Deposition of cadmium and chromium onto test specimens; selection of two aircraft components (in consultation with NRL) for coating; rig testing of coated components-Cherry Point Naval Aviation Depot (CPNAD).

In addition, in the latter stages of the project, attempts would be made to perform actual flight tests on coated and surface modified components. The arrangements for these would have to be made in cooperation with the Army Aviation Systems Command and the Naval Air Systems Command.

An important issue in developing new types of coatings in any system is whether it will have any effect on other system components. As an example, a part that is currently chromium-plated may be sliding contact with another part in the aircraft engine. If the chromium coating is replaced with another coating which demonstrates superior performance in laboratory tests, will it have a detrimental effect on its mating part? This potential problem will be considered in the selection and evaluation of actual components. This program is considered to be of medium technical risk.

**Expected Payoff:**

There are an extremely large number of potential users of the technology developed under this program. Virtually all military installations that overhaul aircraft, land vehicles, or ships perform chromium and/or cadmium electroplating. In addition, many OEM's can benefit from this technology since chromium and cadmium are still being applied to components during the manufacturing process. It is also intended to spin-off this technology into areas related to armaments, e.g. gun tubes, which are routinely electroplated with chromium to provide wear resistance to portions of the bore.

The costs of the alternative coating technologies should not be compared with the previous cost of chrome and cadmium plating, but with the expected future costs associated with the processes, taking into account regulations projected into the future. The Basic Industry Research Lab has performed a detailed cost analysis based on information provided by CCAD and McClellan AFB and on their own calculations related to PVD coating operations and have concluded that for operations that would produce equivalent throughput, the total annual operating cost for a PVD facility would be approximately 20% less than for a plating operation.

Another point that is that there exists the possibility that the coatings developed under this project will demonstrate performance that exceeds that of electroplated coatings, thus reducing the frequency of rework necessary. This will further reduce the costs associated with the new processes.

**Milestones:**

Test coupon fabrication, coating application to coupons, component selection	FY93
Evaluation: lab wear, lab electrochemical, fatigue, salt-spray; coating selection coating optimization identification	FY93-94
Coating components, rig testing	FY94-95
Develop transition plan, flight testing	FY95

**Transition Plan:**

Based on the results of the work under this project, a detailed transition plan would be developed early in 1995, in cooperation with the field activities, CCAD and CPNAD. There would also be coordination with the other activities such as Army's MSC's and RDEC's, NAWC's as well as the Joint Technology Exchange Group and the Aerospace Chrome Elimination Group (government and industry). Additional components beyond those evaluated in the project would be selected and a pilot-production quantities of all components would be coated, with some subjected to additional rig testing (e.g., engine evaluations on a test stand) and the remainder installed in actual operating aircraft. Cherry Point NAD expects to install a large PVD coating system in a January-February 1995 time frame, which will coincide very well with transitioning of the technology. Since it obviously will not be possible to individually evaluate the replacement coatings for every component

that is currently electroplated, a key aspect of the transition plan would be to provide information and data, including coating deposition specifications, to agency engineers so that the new coating technologies can be certified for use in broad areas.

**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
Corrosion Science Group, ARL	240	270
Surface Modification Branch, NRL	245	280
Total	485	550

From these amounts, funds would be provided to the other organizations listed in the previous task listing. Their amounts would range from \$10-30K per year for each organization. It is anticipated that approximately 75% of the total funding would remain in-house at ARL and NRL, with the remaining 25% distributed to the other organizations. Other agencies would be solicited to supplement the SERDP funding.

**Performers:**

See Tasks and Activities. Since there is intended to be a mutual sharing of information between this project and the DARPA project, in which General Electric Aircraft Engines Division and Cummins Engine Company will be participating, and since many OEM's are facing the same hazardous effluent emission restrictions as military installations, it is believed that by the time of completion of this program, there should be a strong possibility for implementation of CRDA's with some of the OEM's.

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Recovery/Recycling/Purification of Plating/Cleaning Baths**

#### **Problem Statement:**

Electroplating shops use process solutions containing hazardous materials for plating, acid etching pickling, alkaline electrocleaning, chromating, anodizing, and other metal finishing operations. The effective life of metal finishing process solution is limited by the increasing levels of contaminants that are drug in from the parts being plated or cleaned. In electroplating baths, these materials may include machining particulates, lubricating oils and solvents from incomplete cleaning of the part prior to the electroplating process; metals drug in from incomplete rinsing of a part during prior process steps or from bus bars; and other ionic species that may accumulate from solution degradation and secondary reactions occurring in the electroplating process. In metal cleaning and stripping baths, both metal and organic contaminants accumulate as they are removed from the part. These contaminants reduce plating and cleaning efficiency, thereby decreasing production rates and increasing current requirements, and will eventually adversely affect the quality of the metal finishing operation. As a result of this contamination, the "spent" bath must be periodically dumped.

Metal cleaning/finishing operations at Navy plating shops alone generate over 500K gal/yr of concentrated hazardous wastes from process solutions that become spent due to buildup of contaminants.

Disposal costs exceed \$2M/yr and will escalate as stricter disposal regulations are imposed. Techniques need to be developed to continuously remove contaminants that buildup in these solutions to prolong process bath life, thus minimizing loss of chemical values and hazardous waste generation from these operations. The goal of this effort is to evaluate purification/rejuvenation technologies, such as electrodialytic membrane separation, electrophoresis, ion exchange, carbon absorption, reverse osmosis, electrochemical reactors, electrodialysis, Donnan dialysis, and ultrafiltration for use in removing contaminants from plating/metal cleaning process baths.

#### **Project Description:**

The objective is to develop innovative techniques for prolonging process bath life and for recycling hazardous materials from spent process baths. The Navy effort was initiated in FY91. In previous work, the waste types generated from spent process baths were characterized and alternative technologies that should be developed for purification and recycling were investigated. A Navy Initiation Decision Report (IDR) was prepared that examined the problems, assessed the state of technology in bath purification and recycling, and identified alternative technologies that could be developed.

In this phase of the program, laboratory and field testing of separation technologies such as electrodialytic membrane, Donnan dialysis, ion exchange, carbon absorption, and ultrafiltration will be conducted to develop the techniques for application to DoD plating shops. Technologies will be identified for both laboratory and field testing based on the DoD matrix of process solutions, the contaminants to be removed, and state of technology.

Testing and evaluation on various process solutions will be performed to determine effectiveness and to optimize design and operational parameters for each purification systems as needed for specific process baths. T&E efforts will need to be prioritized based on DoD waste reduction and cost savings as required to meet DoD/EPA requirements within the scope and budget of the program. Appropriate planning, design, operation, and maintenance criteria will be developed for technology transfer of each system to DoD and private industry plating operations.

Concurrently, destruction technologies for removal of residual organic contaminants will be investigated. Research efforts by the Department of Energy (DOE) and the U.S. Army will be evaluated for application in the elimination of organic contaminants in plating/metal cleaning baths. A demonstration system will be designed based on the most promising technologies and applied to an existing industrial operation. Data will be collected and analyzed on the effectiveness and efficiency of the system which will be used to develop technology transfer documentation.

#### **Expected Payoff:**

Development and demonstration of recycling/purification technologies will provide in-process treatment of plating, acid etching, pickling, alkaline electrocleaning, chromating, anodizing, and other solutions. Hazardous wastes generated from metal cleaning, etching, stripping and electroplating could be reduced by 75% with the extension in process bath life. Navy wide hazardous wastes could be reduced by 375,000 gal/yr providing a savings of \$1.3M per year or more, depending on the cost for disposal. DoD-wide saving would be at least tripled. Users include Navy and DoD plating shops as well as many potential users of this technology in the public and private sectors.

#### **Milestones:**

The following is a schedule of milestones accomplished and planned. Work was interrupted in FY92 due to SERDP funding cutoff, causing a delay in initiation of feasibility studies. Planned work for FY93 through FY95 will involve a joint effort with RREL, U.S. Army, and U.S. Air Force.

- |  |           |
|--|-----------|
| 1. Survey Navy Plating Shops to Establish System Matrix  | Completed |
| 2. Conduct Technology Assessment and Prepare IDR   | Completed |
| 3. Collect Data for Army/Air Force Plating Shops to Establish DoD System Matrix of Process Solution Contaminants   | FY93      |
| 4. Conduct Technology Assessment of Organic Destruction Methods  | FY93      |
| 5. Conduct Feasibility Studies (as appropriate) on Selected Technologies for Purification of Various Solutions, i.e.: Chrome Baths; Cyanide Baths; Nickel Baths; Acid Cleaning Solutions; Alkaline Cleaning. | FY93-94   |

6. Conduct Onsite Test and Evaluation of Purification  
Systems for various solutions

FY94-95

7. Develop Technology Transfer Documentation

FY95

**Transition Plan:**

Documentation covering planning, procurement, design, operation, and maintenance of both purification systems (separation and destruction technologies as developed for specific applications) will be prepared for technology transfer to Navy and DoD activities. This technology transfer package will be published as a final deliverable. The documentation will be provided to appropriate Navy, Army and Air Force activities for implementation including the Air Force's System Program Office the Technology Transfer Division of the Air Force's Center for Environmental Excellence. Private industry will have access to the information developed and, with it will be able to apply the technology as desired. The capabilities of EPA's Center of Environmental Research Information (CERI) will be used to promote technology transfer to the private sector.

**Funding: (\$K)**

FY93	FY94
600	800

**Performers:**

NAVY/NAVFACENGCOM/NAVCIVENGRLAB (NCEL) jointly with the Risk Reduction Engineering Laboratory (RREL), U.S. Army, and U.S. Air Force.

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**SERDP Thrust Area:** Pollution Prevention

**Title:** Solid State Metal Cleaning

**Problem Statement:**

The goal of this project is to develop innovative metal cleaning processes that do not require the use of water or volatile organic compounds (VOCs).

Cleaning of metals is a mandatory step in the processing of aircraft components, including wing skins, fuselage panels and bulkheads, etc., prior to surface preparation, such as anodizing, and subsequent priming in preparation for coating or adhesive bonding. State-of-the-art cleaning processes now involve the use of PD 680 type solvents, chlorinated solvents, or water-based cleaning systems to remove oil, waxes and particulates from the surface of component surfaces.

This is a new project for FY93 SERDP.

**Project Description:**

There are two technical objectives to be achieved by this project:

- (1) To develop and transition to a using customer a cleaning process for large (and small) aircraft components that do not require the use of water or VOCs.
- (2) To develop a process that will allow components to proceed directly to the next step in the process for surface without the need for subsequent treatments involving water or organic solvents.

Research and development (R&D) will be performed to study the mechanisms and kinetics of solid state soil (oils, waxes, particulates and metallic oxides) removal processes. Various processes will be studied including activated particulates or polymers, carbon, starch, CO<sub>2</sub> and various inorganic particulates including carbonates and phosphates. Studies will include assessment of how clean components really need to be before they proceed to the next step in their particular processing track. Components proceeding to inspection or other intermediate process steps do not have to meet the cleanliness standards required for surface preparations such as alodine and anodize or those going into a plating or metal deposition process. Laboratory testing will be accomplished to define and measure surface cleanliness levels needed for various subsequent processing steps in order to maintain/improve the performance of subsequent operations.

The following are tasks associated with this project:

- 1) Experiments to define/delineate mechanisms/kinetics of solid state soil particulates and oxides removal as a function of cleaning media, energy levels, temperatures and times, etc.
- 2) Process studies to select/optimize cleaning process parameters and influence on substrates, mechanics, and physical properties.

- 3) Studies to define, measure and validate cleanliness levels required for components proceeding to the next stop of their process track.
- 4) Testing and analysis to validate that processing changes do not degrade components performance. Factors such as corrosion resistance, coating adhesion/ performance, adhesive bond durability/strength and metal plating adhesion/performance will be comprehensively studied.
- 5) Scale-up to pilot size process to determine scalability of processing parameters previously established.
- 6) Demonstrate/validate process on customer-designated components. Establish and approve process specifications and standards. Perform life cycle cost analysis on process.
- 7) Transition prototype to user/customer for extended production evaluation.

Feasibility studies have been performed using activated carbon/starch/CO<sub>2</sub>/air and other cleaning media for the removal of various types of soil and particulates. Preliminary research has established the feasibility of this approach for the removal of a number of oily, waxy and particulate contaminants.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort will also enable reduction of risks, costs and liabilities associated with use of toxics, and handling, treatment and disposal of hazardous wastes. The project will assist in meeting Air Force pollution prevention objectives to reduce volatile air emissions by 50% by the end of 1999 (1993 baseline).

No government sponsored work is presently ongoing/planned in this technology area.

Technical issues that will need to be addressed include:

- 1) Removal of soils/contaminants from simple/complex geometry components without using liquid.
- 2) Ability of solid cleaners to provide wide spectrum cleaning capability under conditions not detrimental to substrate.
- 3) Develop a safe, environmentally sound and affordable/economical process.
- 4) Obtain adequate cleanliness levels in order to eliminate the need for follow-on cleaning operations.

#### **Expected Payoff:**

If successful, the scope of this effort will cover the gamut of industrial cleaning operations used throughout the industrialized world. Water waste streams and VOC emissions will be eliminated from industrial cleaning operations.

The goal will be to do at least the same (if not better) cleaning job that is now being accomplished using liquids, at a cost equal to or less than today's cost (with no waste streams).

**Milestones:**

Project initiation/start date.

FY93

July

Initiate experiments to select cleaning media and define process mechanisms, and critical process parameters.

FY94

May

Complete media testing and process parameters definitions.

Initiate process parameters optimization and substrate sensitivity testing.

Initiate experiments to define, measure and validate surface cleanliness levels required.

Complete process sensitivity studies and substrate sensitivity testing.

Sep

Initiate coating, bonding plating performance validation studies.

Complete process optimization and initiate scale-up and assemble pilot size process.

Nov

FY95

Optimize and demonstrate pilot scale operation in cooperation with user/customers.

Apr

Complete all performance testing. Write up draft specifications and standards.

Aug

Transfer prototype to user/customer for extended production operation.

**Transition Plan:**

This research and development (R&D) program will be conducted in concert with the Air Logistic Centers and will provide engineering data and process information to allow each user to design and implement a systems and processes which will meet their specific requirements.

Potential users will be an integrated part of the R&D team so that their inputs will be incorporated on a continuous basis into the product development cycle.

**Funding: (\$K)**

FY93

350

FY94

1000

**Performers:**

The project will be performed under the technical leadership and direction of the following:

Air Force Material Command

Aeronautical Systems Center

Wright Laboratory

Materials Directorate

Wright-Patterson AFB, OH 45433

The Materials Directorate will award one or more research contracts to industry to perform the development and integration.

To facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans on having the demonstration site to be either an Air Force Material Command Air Logistics Center or the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB Ohio.

**Technical Point of Contact:**

T. J. Reinhart  
WL/MLSE  
Wright-Patterson AFB, OH 45433  
TEL: (513) 255-3691  
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**SERDP Thrust Area: Pollution Prevention**

**Title: Noncyanide Strippers to Replace Cyanide Strippers**

**Problem Statement:**

The goal of this project is to develop a technical data package for alternative noncyanide stripping solutions.

The organizations targeted for this project are the Air Force Air Logistic Center maintenance operations, other AF major command maintenance activities, other DoD maintenance organizations and private sector industrial operations could benefit from this research.

Cyanide strippers used to remove various metal platings from substrate metals platings are dangerous to users health and the environment. Cyanide strippers contribute to the wastes which must be treated at the industrial waste treatment plant. Air Force electroplating shops have been given Notices of Violation by the EPA for discharging complex cyanides.

This is a continuation of a project started in FY 92 but stopped due to lack of funds in FY 93.

**Project Description:**

The technical objective of this project is to validate that the noncyanide baths being developed to replace cyanide baths do not create any long range detrimental effects on the properties of the treated metal. A related objective is to develop a generic metal stripping bath that would eliminate the necessity to dump complete baths when additional cyanide is needed due to the incompatibility of a "new" vendors product with the previous one.

This program will take the previously developed noncyanide strippers and the test results from stripping silver with noncyanide baths and apply them to all other metal stripping applications. Also, biological destruction systems for the waste noncyanide baths will be tested and verified. Full-scale demonstrations are planned for an Air Force Material Command installation. The final product will be a technical data package for new chemical strippers.

This project supports the Tri-Service requirements, "Non-hazardous alternatives for cyanide in electroplating operations" (PP-I-3-H).

**Expected Payoff:**

This program will reduce cyanide wastes with their associated handling problems and disposal costs from electroplating shop operations. Based on projected costs of a treatment system and the potential savings in chemical handling, it is estimated that an eight month return on investment would be realized.

**Milestones:**

Complete Technical Report/Users Manual from Chemical  
Development and Initial Tests

FY 93  
Apr

Complete analysis of Demonstration Project

Jul

Publish Final Test Report

Sep

**Transition Plan:**

Following completion of the demonstration, the technical data package describing the operational criteria and optimized technology developed during the research will be transitioned to AF users for individual procurement of new chemicals. The Air Force Center for Environmental Excellence's Technology Transition Division will be continually advised of the status of this research and will assist in the transition throughout the Air Force, to other federal agencies, and to the private sector.

**Funding: (\$K)**

FY93  
1100

**Performers:**

Primary USAF POC: AL/EQVS:  
Lt. Phil Brown  
TEL: (904) 283-6018  
FAX: (904) 283-6004

A contract with the Department of Energy and their contractor, EG&G Idaho, Idaho Falls, Idaho will be used.

**Technical Point of Contact:**

AL/EQVS, Lt. Phil Brown  
139 Barnes Drive  
Building 1117  
Tyndall AFB, FL 32403-5319  
TEL: (904) 283-6018  
FAX: (904) 283-6004

## **SERDP Thrust Area: Pollution Prevention**

**Title:** Alternative Process to Acid Cleaning/Degreasing of Depleted Uranium

### **Problem Statement:**

Conventional methods of removing surface oxides and contaminants from depleted uranium (DU) components have historically involved acid cleaning. This can lead not only to generation of mixed hazardous waste but also raises concerns regarding in-plant personnel safety. The goal of this effort is to demonstrate the capability of alternate cleaning processes to that of acid cleaning and to implement those processes into applicable areas of Kinetic energy penetrator manufacturing and also requirements identified within the demilitarization or recycle of DU components and ancillary contaminated hardware. This effort will benefit all DoD agencies involved with DU components. This project is a new approach associated with the life cycle of Kinetic energy penetrator munitions.

### **Project Description:**

The objective of this study is to qualify alternate cleaning methods. Frozen carbon dioxide (CO<sub>2</sub>) or argon (Ar) grit blasting and water jet techniques will be explored. Frozen CO<sub>2</sub> and/or Ar pellets will be used to grit blast oxidized DU surfaces. The DU to be studied will include penetrators representative of what we would expect from demilitarization operations and also machining chips, which can be expected to be heavily oxidized. High efficiency particulate air filtration will be employed to contain the removed oxide within the working chamber. The advantage of this cleaning technique is that the frozen pellets sublime, creating no additional waste which has to be dealt with. Water jet cleaning will also be investigated. This technique is more aggressive than the bombardment of frozen gases and therefore may be an appropriate selection in certain instances.

Frozen CO<sub>2</sub> pellet grit blasting is being used in industry and by the Air Force to strip paint. The Army is also looking at this process as a means of extracting explosives from projectile cavities.

This project is assessed as being low to moderate in technical risk for the applications which are to be investigated.

### **Expected Payoff:**

Eliminate the generation of mixed hazardous waste.

### **Milestones:**

1. Develop cleaning requirements and acquire samples - 4 months after start.
2. Evaluate system parameters and proveout with existing equipment - 10 months after start.
3. Build prototype equipment and system proveout - 22 months after start.
4. Purchase and installation of production equipment - 36 months after start.

**Transition Plan:**

This project is included in the DoD Strategic R&D Plan and is depicted on roadmap # 3.C/DU Waste Elimination.

The Coordinator between user and performer was accomplished during a pollution prevention user review in Jul 92, a peer review in Aug 92 and the recent DoD Strategic Environmental R&D review during 7-11 Dec 92.

Briefings to Government and Industry audiences were given at the ADPA environmental symposium at Picatinny Arsenal, 20-21 Oct 92 and the AMCCOM Advanced Planning Briefing to Industry 28-29 Oct 92 at Rock Island, IL.

**Funding: (\$K)**

FY93	FY94
125	225

**Performers:**

DOE (Oak Ridge Y-12 Plant/Idaho National Engineering Lab), Penetrator Manufacturer.

**Technical Point of Contact:**

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US ARDEC  
Materials & Aeroballistics Technology Division  
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## **SERDP Thrust Area: Pollution Prevention**

**Title:** Non-Chromatic/Non-Carcinogenic Etching for Bonded Structures

### **Problem Statement:**

The dramatic growth for strong, durable, lightweight structures for both military and commercial applications has placed an ever-increasing reliance on adhesively bonded structures as compared to mechanically fastened joints. Unfortunately, in order to obtain an acceptable level of strength and durability in bonded structures, surface chemistry of substrates to be bonded must be altered, and in many cases, the processes used pose significant problems in worker health and hazardous waste management. The Army has adopted a pollution prevention hierarchy which has source reduction/material substitution as the most desirable approach to minimizing hazardous waste generation. This project focuses upon reducing hazardous waste generation by investigating the use of new surface preparation techniques prior to adhesively bonding both metallic and advanced fiber-reinforced composite structures. The P2 etch, for example, developed at Armament Research, Development & Engineering for use on aluminum alloys, is a non-chromated, non-carcinogenic process now adopted by aerospace firms such as Piper and tactical shelter manufacturers for other metals (e.g., titanium and stainless steel) and fiber-reinforced composites. This project's objective is to investigate the feasibility of extending P2 etch as well as other "LoTox" process technologies to treat engineering materials which currently involve environmentally unsafe chemicals and expensive waste handling procedures, while maintaining functional levels of adhesive bond strength and durability.

### **Project Description:**

Adhesive bonding is integral to nearly every item in the Army's inventory, including large and small scale calibre ammunition, mines, missiles, armored vehicles, tactical shelters, helicopters, etc. This project's benefits are difficult to quantify; however, the Army should be able to achieve technical, financial and environmental results. Environmentally, hazardous waste generation will be reduced and an associated benefit of reducing worker exposure to hazardous materials will be achieved. Costs will be reduced since less hazardous waste will be generated and savings from reduced repair and maintenance through increased level of part reliability will be realized. New adherents will result in improved quality of adhesively bonded structures.

The initial technical approach will involve the study of chemical and rheological effects of the P2 etch and various other "LoTox" alternatives developed on titanium and fiber reinforced thermoplastic/thermoset composite surfaces. Processes will be evaluated based upon waste stream analysis, health and safety considerations, and resulting adhesive bond performance. Subsequent project efforts will address the most promising "LoTox" methods, concentrating on optimizing process parameters for scale-up to a pilot-plant.

### **Expected Payoff:**

It is expected that this project will result in the modification of existing adhesive technology to reach a new plateau in environmentally acceptable adherents.

**Milestones:**

Develop LoTox processing for metal/composite substrates. Perform chemical and rheological studies.	FY 93
Conduct functional tests/waste analysis. Identify most promising LoTox processes.	FY 93-94
Optimize LoTox processes on pilot plant scale/develop recommendations for scale-up to production	FY 94

**Transition Plan:**

The technologies developed and proven in this project will be made known through bulletins, reports, and articles for leading industrial manufacturing publications.

**Funding: (\$K)**

The total project funding from SERDP to complete this demonstration is \$1,150,000. Below, this figure is separated by fiscal year, by total and by in-house governmental personnel.

	FY93	FY94
SERDP	350	800
Service Funds	100	400

**Performer:**

U.S. Army  
Armament Research Development and Engineering Center  
SMCAR-AEE  
Picatinny Arsenal, NJ

**Technical Point of Contact:**

Mr. Joseph Brescia  
U.S. Army  
Armament Research Development and Engineering Center  
Picatinny Arsenal, NJ 07806-5000  
TEL: (201) 724-4555  
DSN: 880-4555

## **SERDP Thrust Area: Pollution Prevention**

### **Title: Electroplating Waste Reduction**

#### **Problem Statement:**

To replace hazardous plating processes (chromium, cadmium, cyanide, etc.) currently used on Naval aircraft, weapons platforms and ground support equipment. Chromium and cadmium are heavy metal pollutants and carcinogens. Cyanide is hazardous to human health. The Clean Air Act, as well as other EPA and state Departments of Environmental Resources regulations restricted the emissions from these processes. In addition, OPNAVINST and CNO directives require reductions in hazardous waste. Presently, these plating processes are used in production and Depot level maintenance operations. Therefore, in order to comply with these regulations while maintaining aircraft performance and operational readiness, alternative plating processes need to be developed and validated.

#### **Project Description:**

Chrome plating and cadmium plating are common inorganic corrosion preventive coatings. Chrome plating is also used to build up worn components when they no longer meet tolerance levels. Cadmium plating is frequently used for fasteners and other very tight tolerance parts because of the dual qualities of lubricity at minimal thickness and superior sacrificial corrosion protection. Replacements for chromium and cadmium will require similar mechanical and performance properties over the full spectrum of applications for which they are currently used. One alternative to Cad plating which has potential to fulfill all of these requirements is aluminum-manganese electroplating from a molten salt bath. This process differs from the traditional aqueous electrolytic plating bath. The best aluminum-manganese (Al-Mn) concentrations for Naval aircraft use will be isolated through a test program which examines the varied choices of Al-Mn systems on test coupons of various materials and sizes. This bath formulation will then be established as a full-size prototype at a selected NADEP. Following full-scale tests Al-Mn will be transitioned to the fleet through specification modification and design changes. In addition, ion vapor deposited (IVD) aluminum is another demonstrated alternative for certain applications that will be pursued for Navy use. Other alternatives to hexavalent chrome plating and cadmium plating include: electroless nickel plating, hard chrome plating, tin-zinc plating, zinc-nickel plating. In addition, alternative application techniques with non-chrome/cadmium materials (physical vapor deposition, spray casting, flame spray/high velocity oxygen fuel, etc.) will be investigated. Finally, cyanide strippers have been used to remove metallic coatings. Non-cyanide strippers will be evaluated based on an Air Force investigation.

#### **Expected Payoff:**

The elimination of chromium and cadmium plating significantly reduces the total amount of hazardous materials emitted from Navy operations. Elimination of chrome plating also eliminates the need for expensive emission control equipment required by CAA and AQMD legislation (estimated at several \$M per Depot facility). Furthermore, these alternatives significantly reduce disposal costs of chromium and cadmium from Navy operations. This effort is in direct support of Navy and DoD hazardous waste minimization

policies/directives. In addition, without the use of adequate replacements, aircraft operational readiness could be curtailed by excessive environmental degradation. This is particularly important considering the cost of Navy A/C, weapon systems and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also be transition to many areas of the commercial sector (airlines, automotive, equipment manufacturers, fastener manufacturers, etc).

#### Milestones:

Initiate Al-Mn Investigation	FY93
Demonstrate IVD aluminum	
Initiate Physical Vapor Deposition Investigation	
Hard Chrome Plating Technology Transfer	
Initiate Electroless Ni Investigation	
Evaluation of Al-Mn Electroplating	FY94
Electroless Ni Optimization/Demonstration	
Physical Vapor Deposition Evaluation	
Demonstration of Al-Mn Electroplating	FY95
Implementation of Electroless Ni	
Physical Vapor Deposition Optimization	
Initiate Spray Casting Investigation P	
Implementation of Al-Mn Electroplating	FY96
Physical Vapor Deposition Service Demonstration	
Optimize Spray Casting Process	
Investigate Non-Cyanide Metal Strippers	
Implementation of Physical Vapor Deposition	FY97
Service Demonstration of Spray Casting Process	
Service Demonstration of Non-Cyanide Metal Strippers	
Initiate Flame Spray/HVOF Investigation	
Implementation of Spray Casting Process	FY98
Implementation of Non-Cyanide Metal Strippers	
Optimize/Demonstrate Flame Spray HVOF Processes	
Investigate Zn-Ni and Sn-Zn Electroplating	
Implementation of Flame Spray/HVOF Processes	FY99
Service Demonstration of Zn-Ni and Sn-Zn Electroplating	
Implementation of Zn-Ni and Sn-Zn Electroplating	FY00

**Transition Plan:**

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP and transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination throughout the development and evaluation of these materials will ensure availability for implementation.

**Funding: (\$K)**

FY93	FY94
460	370

**Performers:**

Evaluation/demonstration of Chromium and Cadmium Plating alternatives is being performed by the Naval Air Warfare Center Aircraft Division Warminster, Naval Aviation Depots and the Maintenance Technology Center for Environment. This effort is being coordinated with the Air Force (Tinker ALC, Tyndall AFCEA), the Army, and aerospace industries (Boeing, Rohr, Grumann, MCAIR, etc.).

**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

**Title:** In-Tank Treatment of Acid and Alkaline Cleaners

### **Problem Statement:**

Large quantities of hazardous waste are generated at metal finishing operations throughout the Army's industrial base. In 1990, Army Materiel Command installations combined to produced 1,469,961 kilograms of metal finishing hazardous waste (reference: Army Material Command, Hazardous Waste Minimization Program, Progress Report 1990, pub. November 1991). In order to investigate a possible solution to minimizing this generic waste type, a project is proposed for the Anniston Army Depot (ANAD) to investigate ways to increase their in-process treatment efficiency. The target waste stream consists of alkaline cleaner and hot rinse which are generated from the metal heat treatment operations.

This project will investigate a batch in-tank treatment process that will yield effluent that is more suitable for subsequent Industrial Wastewater Treatment Plant (IWTP) treatment. The results of this investigation will be transferable to across the Army's industrial base, e.g., Anniston AD, Watervliet Arsenal, etc.

### **Project Description:**

The revised Clean Water Act (CWA) has required more stringent discharge standards to be met by all IWTPs. It is predicted that many Army installations will be unable to meet these new stricter National Pollutant Discharge Elimination System (NPDES) standards because the standards exceed the IWTP's ability to attenuate the waste. Violations of these standards can result in both monetary fines and adverse publicity to that Army installation issued a Notice of Violation. Currently, many IWTPs have reduced their wastewater treatment costs and increased their process removal efficiency by installing new, more efficient pretreatment process systems. These pretreatment systems have become an integral part of the treatment process in order to meet the NPDES requirements. Finding innovative ways to reduce waste at the source before it enters the Army installations' IWTP will require new technology(s) to be investigated. The value of this project is its focus on batch treatment which is more typical of the Army's production when compared to the treatment techniques used at continuous large-volume plants.

This project's technical approach is to develop an in-tank treatment procedure from the results of the bench scale testing. Bench scale testing will focus upon the elimination or removal of wastewater constituents that are potentially disruptive to the IWTP process. The constituents which will be targeted are pH, emulsified oil (alkaline corrosion removal) and compounds such as phosphates that interfere with flocculating and settling (alkaline corrosion remover and phosphoric acid). Bench scale tests will involve several processes for constituent removal, including pH adjustment, emulsion breaking, and precipitation. The final effort of this investigation will consist of an in-tank treatment process design and evaluation of a batch treatment system that can be integrated in the actual process tanks. Mechanical mixers will be evaluated for agitation and concentrated treatment chemicals will be used for full scale in-tank treatment evaluations. A final report detailing the test results and a procedure for implementation will be prepared.

**Expected Payoff:**

It is expected that this project will demonstrate that batch in-tank treatment process is a viable option for treating hazardous waste in an economical manner. The anticipated financial benefits are calculated to be \$40,000 per year at Anniston AD and \$12,000 per year at Watervliet Arsenal for a cumulative Army savings of \$52,000 per year.

**Milestones:**

The tasks/milestones are shown below for the life of the project:

Develop Test Plan, Conduct Bench Scale Tests	FY93
In-tank Treatment Process Design & Evaluation	FY94
Conduct Full Scale Tests, Prepare Technical Report, etc.	FY94

**Transition Plan:**

The technology developed and proven in this project will be made widely known through bulletins, reports, and articles for leading environmental publications. This project's results will be made available especially to those DoD installations that treat heavy metals.

**Funding: (\$K)**

	FY93	FY94
SERDP	250	305
Service Funds	90	122

**Performers:**

U.S. Army, Anniston Army Depot, Anniston, AL

U.S. Army, Watervliet Arsenal, Watervliet, NY

US Army, Armament Research, Development and Engineering Center, Picatinny Arsenal, NJ

**Technical Point of Contact:**

The following engineer may be contacted concerning this project:

Mr. Tim Garrett  
Anniston Army Depot  
Anniston, AL 36201  
TEL: (205) 235-6350  
DSN 571-6350

## **SERDP Thrust Area: Pollution Prevention**

**Title:** Alternative Paint Stripper for Powder and Electrodeposition Coatings

### **Problem Statement:**

Identify or develop alternative chemical paint stripper formulations which will remove powder and E-coats while minimizing pollutant discharge, other environmental and worker health risks, and disposal liabilities.

### **Project Description:**

There is a need for alternative chemical paint strippers to minimize objectionable environmental pollutant discharges, environmental disposal liabilities, and other environmental and worker health impacts. Alternative paint strippers for powder and cathodic electrodeposition (E-coat) coatings are not yet available. These coatings are particularly difficult to remove when it is required to do so for maintenance. Based on depot community needs, stripper materials sensitive to Army needs for stripping powder and E-coat paints will be identified from commercial sources, if available, or formulated. Methods will be developed and the new materials will be evaluated for performance and environmental and health hazards. Pilot scale tests for performance and environmental monitoring will be conducted at cooperating depot. Successful formulations will be identified for depot use.

### **Milestones:**

Identification of commercial stripper material or formulation of	FY 93
Material evaluation	FY 94
Field testing at depot and specifications developed	FY 95

### **Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
SERDP	190	195
Service Funds	190	195

### **Performers:**

CERL, Champaign, IL, Depots to be determined.

### **Technical Point of Contact:**

Dr. Keturah Reinbold  
Natural Resources Division, Environmental Sustainment Laboratory  
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## **SERDP Thrust Area: Pollution Prevention**

**Title:** Environmentally Acceptable Heat Treating

### **Problem Statement:**

To eliminate the environmental problems which are associated with standard commercial heat treatment/quench systems which use molten salt/metal, oil, and water base solutions to thermally process DoD materials and components. To establish fluid bed heat treating as an environmentally benign process for the broadest spectrum of thermal processing schemes utilized by DoD agencies in the manufacturing of metal components.

### **Project Description:**

The fluid bed furnace/quench system presents a unique environmentally benign, cost effective heat treating method that can be readily adapted to a wide range of military and industrial processing needs. Incorporation of this heat treating technology would ameliorate the environmental problems that make the more traditional heat treating methods unacceptable in today's manufacturing climate. By eliminating the more traditional heat treatments that generate hazardous waste, this project aims at implementing "zero waste" manufacturing procedures in developing thermal treatments for Army metal components.

The initial technical approach will accomplish the following: clarify the principle heat treatment concepts of fluid bed thermal processing, provide guidelines for the selection and use of fluid bed furnaces in the heat treatment of metal armament components, undertake to incorporate fluid bed thermal processing as an integral part of the design and manufacturing process for metal armament components utilizing basic considerations of statistical process control and concurrent engineering, coordinate with National/International thermal processing associations to develop common processing standards, specifications, and quality assurance (ISO 9000) standards.

Subsequent project efforts will accomplish the following: implement quality assurance standards and ISO 9000 criteria as thermal processing system standards requirement for metal components, develop and implement thermal processing practices for specific armament components and provide corresponding technical data packages.

### **Expected Payoff:**

It is expected that this project will result in the modification of existing manufacturing processes and strive towards a "zero discharge" for metal thermal treatment.

### **Milestones:**

The tasks/milestones are shown below for the life of this project:

Develop Army Test Plan for environmentally safe thermal processing needs;

FY 93

Initiate study to develop fluid bed thermal processing to replace hazardous waste generating practices in present thermal treatment facilities; FY 94

Coordinate National/International Heat Treatment Associations to develop common standards/specifications; FY 94

Implement fluid bed thermal processing practices for specific metal components and provide technical data packages; FY 95-96

**Transition Plan:**

The technologies developed and proven in this project will be made known through bulletins, reports, and articles for leading metal technology trade publications.

**Funding: (\$K)**

The total project funding from SERDP to complete this demonstration is \$1,265,000. Below, this figure is separated by fiscal year, by total and by in-house government personnel.

	<b>FY93</b>	<b>FY94</b>
SERDP	265	325
Service Funds	133	163

**Performer:**

U.S. Army  
Armament Research Development and Engineering Center  
Picatinny Arsenal, NJ

**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Pre-Paint Non-ODC Batch Cleaning**

#### **Problem Statement:**

The manufacture of material requires that specific metallic components be degreased prior to subsequent industrial operations. Specifically, before small caliber bullet tips are painted for identification, they are degreased in batches using a chlorinated solvent, i.e., 1,1,1-trichloroethane. The adverse environmental effects of this solvent have been noted in the EPA's Industrial Toxics Project, a plan with which the Army intends to comply. In addition, this solvent possesses an ozone depletion potential and as such, is included in a United States ban on further production and importation beginning on 31 Dec 95. A DoD Directive, 6050.9, entitled CFCs and Halons, requires that research and development be conducted to reduce or eliminate the DoD's dependence on ozone depleting chemicals. To date, sufficient resources have not been allocated to comply with this 1989 Directive. In addition, this solvent presents specific industrial hygiene concerns as well. The objective of this project is to substitute the solvent degreasing with a more environmentally compliant aqueous based batch type system. It is proposed that an Army installation be selected for the validation, demonstration, and implementation of the alternative cleaning system. Typical aqueous based cleaning systems incorporate heated biodegradable cleaning agents utilized in immersion tanks, with some form of agitation employed. Multiple rinse tanks ensure that the cleaned parts are free from contaminants and cleaning agent residue. Although the rinse water will be heated to facilitate evaporation, forced hot air drying stations will be integrated into the cleaning system. These types of cleaning systems are technically mature and have been proven in the commercial sector. However, adaptation of these systems for certain military unique applications is required. The Army, as well as other DoD components, have conducted limited research and development in this area. This particular endeavor, batch cleaning prior to painting, requires additional resources.

#### **Project Description:**

To meet the technical objective of replacing the solvent cleaning system with one which is aqueous based, different cleaning agents will be tested against standards for level of cleanliness achieved and material compatibility. Each alternative cleaning agent will also be weighed in terms of its environmental and safety characteristics. The appropriate cleaning agents will be matched with the specific types of cleaning equipment leading to equivalent or superior performance when compared to the solvent based system, e.g., agitation vs. ultrasonics. The technical and economic feasibility of each alternative system will be ranked for comparative analysis. The basis for these selections will be derived by an initial data collection effort consisting of a literature review and contact with potential chemical and equipment suppliers. After the laboratory scale analysis has been performed and the list of potential alternatives has been narrowed, pilot scale demonstrations will be conducted either at the Army facility, or at a vendor's site. Final validation of the alternative system will be conducted at the Army site at actual production rates utilizing actual production parts. Information from other ongoing efforts within DoD regarding metal parts cleaning will be used and results shared as this project progresses.

**Expected Payoff:**

Substitution of chlorinated solvents will result in compliance with DoD and Army policy and the elimination of a portion of the Army's contribution to the concentration of stratospheric chlorine. Also eliminated will be the expense of the increasingly costly solvent and the generation of its associated hazardous waste. Elimination of this solvent will facilitate the Army in meeting its goal to reduce the amount of hazardous waste generated by 50 percent of 1992 quantities by 1995. Continued reliance on 1,1,1-trichloroethane will adversely impact material production when its supply becomes scarce.

**Milestones:**

		Completion Dates (Months after receipt of funding)
Task I -	Literature Research/Vendor Survey	5
Task II -	Laboratory Scale Analyses	11
Task III -	Pilot Scale Analyses	19
Task IV -	Production Trial	24

**Transition Plan:**

This project begins as a technology demonstration effort and transitions to implementation upon completion of the production trial tests. The performer will provide technical documentation regarding the results of the project to other potential users. Coordination between the performer and potential users will be accomplished through technical presentations and through technical reports and articles distributed by various centers for technical excellence. Previous coordination was accomplished during a pollution prevention user review in July 1992, a peer review in August 1992, and the recent DoD Strategic Environmental R&D review during 7-11 December 1992. Briefings to Government and industry audiences were given at the APDA Environmental Symposium at Picatinny Arsenal, 20-21 October 1992, and the AMCCOM Advanced Planning Briefing to Industry 28-29 October 1992 at Rock Island, IL. A roadmap of this transition plan is included in the DoD Strategic Research and Development Plan Program under 3.G.

**Funding: (\$K)**

		FY 93	FY 94
Task I -	Literature Research/Vendor Survey	45	
Task II -	Laboratory Scale Analyses	80	10
	In-House	25	
Task III -	Pilot Scale Analyses		130
	In-House		25
Task IV -	Production Trial		165
Total		150	330

**Performers:**

The U.S. Army Armament Research Development and Engineering Center will serve as the managing organization for the project, relying in part on the expertise of the engineering staff at the Army's Center for Technical Excellence for Chlorinated Solvent Replacement, located at the U.S. Army Red River Army Depot. Engineering support will also be available from the National Defense Center for Environmental Excellence. It is proposed that the validation, demonstration, and implementation of the alternative metal parts cleaning system be conducted at the U.S. Army Lake City Army Ammunition Plant. Olin Defense Systems Group, the operating contractor at the Government owned facility, will also provide support and resources as required. Various chemical and equipment suppliers from industry will be consulted in an effort to acquire the optimal alternative cleaning system.

**Technical Point of Contact:**

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**SERDP Thrust Area:** Pollution Prevention

**Title:** Investigation of Continuous Aqueous Cleaning System to Eliminate CFCs

**Problem Statement:**

The manufacture of ammunition metal parts requires that specific components be degreased prior to subsequent industrial operations. Specifically, prior to painting large caliber projectile subassemblies, they are first vapor degreased in a continuous operation using a CFC 113-based solvent to remove light water soluble cutting oils and hand oils. Increasing regulatory restrictions and the cost of CFC-based solvents necessitate the implementation of alternative cleaning systems. The proposed technology customer is the Louisiana Army Ammunition Plant.

**Project Description:**

DoD Directive 6050.9 and AMC-R 70-67 require that alternatives to CFCs be sought. The objective of this project is to adapt a continuous type aqueous based cleaning system for use in the large caliber projectile paint line. LAAP and ARDEC have collected data on replacement systems for this application during execution of an Army MANTECH effort.

Regarding the technical approach for this project, (6.3a) specifications for LAAP's cleaning system will be prepared and off-the-shelf equipment will be customized for the paint line.

End Item(s) affected include 155mm projectile metal parts.

**Expected Payoff:**

Substitution of CFC solvents will result in compliance with DoD and Army policy and the elimination of a portion of the Army's contribution to the concentration of stratospheric chlorine. Also eliminated will be the expense of the increasingly costly solvent and its associated hazardous waste. Continued reliance on CFC-based solvents will adversely impact production when the production and importation of CFC-based cleaning solvents is banned beginning 31 Dec 95.

**Milestones:**

	Completion Dates
Select and validate cleaning agent and specify equipment	FY93
Prove-out equipment technology and install at LAAP	FY94

**Transition Plan:**

Technical report, design/purchase specification package, cost analysis.

**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
SERDP	120	475
Service Funds	20	20

**Performer:**

The performers are ARDEC and LAAP.

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**SERDP Thrust Area:** Pollution Prevention

**Title:** Cadmium Plating Alternatives

**Problem Statement:**

Currently, 80 percent of the environmental releases of Cd may be directly related to electroplating waste. More than 50 percent of these discharges may be directly related to wastes generated by DoD plating activities. Objective is to develop, evaluate, and implement alternatives to Cd plate.

**Project Description:**

In addition to these environmental problems, Cd plating is a health hazard to workers operating electroplating baths. This project meets the DA goal of 50 percent reduction in hazardous waste generation by 1995. The technical approach is to select viable candidates, perform laboratory corrosion, adhesion, SCC coefficient of friction, breakaway torques and compare results with Cd plate. Determine effects of co-mingling with Cd and galvanic coupling with steel and aluminum alloys.

**Milestones:**

Laboratory testing of additional alternatives (Ion beam assisted deposition) (Zn-Ni, Al-Zn)	Sep 93
Outdoor exposure tests	Jul 94
Field test	Jul 95

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
270	170

**Performers:**

MTL, TACOM, OCR

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**SERDP Thrust Area:** Pollution Prevention

**Title:** Aircraft Maintenance Chromium Replacement

**Problem Statement:**

The goal of this project is to replace chromates (Cr) currently used in aerospace materials and processes on Navy aircraft, weapon platforms, and ground support equipment. Chromium VI is a carcinogen and Federal agencies, like the EPA, and state agencies, like the California Air Quality Management Districts (AQMD), have begun to restrict the use of this hazardous material. Federal and State regulations limit or prohibit the use of chromate containing materials. Chromate containing materials used in production and depot level maintenance operations have been determined to be a large contributor to waste generation. Therefore, in order to comply with Federal and State regulations, as well as military policy directives, chrome-free alternatives have to be developed.

**Project Description:**

Non-chromate alternative materials and processes will be investigated for current anodizing, pretreating, sealing adhesive and corrosion preventive processes. The approach taken for the development of non-chromate materials will be identification, development, test & evaluation, demonstration and implementation. Chromic acid anodizing (CAA), a common inorganic coating for pretreating aluminum prior to painting, will be used as an example of this approach.

This program will identify the best alternatives to CAA from existing and developmental coating methods. These alternatives include thin sulfuric, phosphoric acid anodizing and Boeing Aerospace Corp's Boric-Sulfuric Acid Anodize. Selected alloys will be processed and tested to determine which replacement systems will provide equivalent corrosion resistance and paint adhesion while maintaining the existing mechanical properties provided by chromic acid anodizing. The most promising alternative will be optimized for aircraft applications. The best alternative process will be demonstrated at the Naval Aviation Depot (NADEP) at North Island. Upon successful completion of the service demonstration, the MIL-A-8625 Anodize specification will be modified and the process will be transitioned to fleet use/implementation. This approach will be taken for the development of non-chromate pretreating materials (alkaline cleaners & deoxidizers, etc.), adhesives, sealants, and other aerospace chrome containing corrosion preventive materials.

**Expected Payoff:**

The elimination of chromic acid anodizing, chromated alkaline cleaners & deoxidizers, and sealants & adhesives, significantly reduces the total amount of chromium emitted from Navy operations. Elimination of chromic acid anodizing also eliminates the need for expensive emission control equipment (estimated at \$4-6M per Depot facility) required by CAA and AQMD legislation. Non-chromated alkaline cleaners and deoxidizers, developed under a PA funded program have already been implemented at two NADEPs to meet these new regulations.

Furthermore, these alternatives also significantly reduce rinsing disposal costs of chromium from Navy operations. This effort is in direct support of Navy and DoD hazardous waste minimization policies/directives. In addition, without the use of adequate replacements, aircraft operational readiness could be curtailed by excessive environmental degradation. This is particularly important considering the cost of Navy A/C, weapon systems and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also transition well to many areas of the commercial sector (airlines, automotive, equipment manufacturers, etc).

<b>Milestones:</b>	<b>STATUS*</b>	<b>FY</b>
Service demonstration & spec revision for non-Cr anodize	P	93
Evaluate non-Cr adhesive pretreatments	P	93
Initiate non-Cr adhesive bond primer development	P	93
Initiate water-borne non-Cr adhesives evaluation	P	93
Implementation of non-Cr anodize	P	94
Optimize non-Cr adhesive pretreatments	P	94
Evaluate non-Cr adhesive bond primers	P	94
Evaluate water-borne non-Cr adhesives	P	94
Service demonstration of non-Cr adhesive pretreatments	P	95
Optimize non-Cr adhesive bond primers	P	95
Optimize water-borne non-Cr adhesives	P	95
Initiate non-Cr sealants developments	P	95
Transition/implementation of non-Cr adhesive pretreatments	P	96
Service demonstration of non-Cr adhesive bond primers	P	96
Service demonstration of water-borne non-Cr adhesives	P	96
Evaluate/optimize non-Cr sealants	P	96
Initiate water displacing corrosion preventatives	P	96
Transition/implementation of non-Cr adhesive bond primer	P	97
Transition/implementation of water-borne non-Cr adhesives	P	97
Service Demonstration & spec revision of non-Cr sealants	P	97
Evaluate water displacing corrosion preventatives	P	97
Transition/implementation of non-Cr sealants	P	98
Service demo of water displacing corrosion preventatives	P	98
Transition of water displacing corrosion preventatives	P	99

\* P = Planned

#### **Transition Plan:**

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP and transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination throughout the development and evaluation of these materials will ensure availability for implementation. For example, non-chromated alkaline cleaners and deoxidizers, developed under the PA funded program, have already been implemented at NADEPs to meet these new regulations. NADEP Jacksonville has reported a cost savings of \$23K and a hazardous waste reduction of

3 tons of chromium waste from the use of the non-chromate deoxidizer material in the first year.

**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
Y817*	130	0
DERA	-	-
SERDP	170	250
TOTAL	300	250

\* POLLUTION ABATEMENT (6.3B)

**Performers:**

Evaluation/demonstration of Chromium-free alternatives is being performed by the Naval Air Warfare Center Aircraft Division Warminster, Naval Aviation Depots and the Maintenance Technology Center for Environment. This effort is being coordinated with the Army Materials Technology Laboratory (Watertown, MA), the Air Force (Tinker ALC and Tyndall AF Civil Engineering Services Center), and aerospace industries (Boeing, Rohr, Grumann, MCAIR, etc.).

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Nonchromate Conversion Coatings for Aluminum Alloys**

#### **Problem Statement:**

The goal of this program is to develop and implement a non-chromate conversion coating for aluminum alloys and an alternative sealing treatment to the currently used sodium dichromate in the anodizing process for use in combat and tactical vehicles, munitions, and aircraft.

Chromate conversion coatings, such as the currently specified alodine treatment, have been identified as a large, unacceptable source of hazardous waste generation and dangerous to worker health and safety. Chromate conversion coatings have been utilized to promote adhesion and corrosion resistance of organic coating systems (primer-topcoat).

Efforts to develop finishing systems that do not incorporate a pre-treatment have not demonstrated comparable performance. This project, which is aimed at reducing production and disposal of hexavalent chromium hazardous waste, received support (\$50K) in FY91 under the EAMTP program but remained unfunded in FY92 and FY93 due to unavailability of funds.

Another source of unacceptable hexavalent chromium is the sodium dichromate seal used in the aluminum anodizing process. Removal and disposal of the additional hexavalent chrome from the process waste water exacerbates the cost and the potential health safety problem. The use of a non-chromate sealing system will permit an anodizer to eliminate one hazardous constituent. This effort has not been funded previously.

#### **Project Description:**

Preliminary laboratory testing at ARL Watertown (previously MTL), based on salt fog and electrochemical impedance spectroscopy, showed that a Sanchem Boehmite non-chromate conversion coating and sealers was promising for several aluminum alloys. The technical objective of the proposed project is to demonstrate the efficacy of non-chromate conversion coatings for aluminum alloys without compromising corrosion resistance. Limited test results of a non-chrome sealer, nickel acetate for anodized aluminum indicated that this seal system could provide comparable corrosion resistance to the chrome sealer. Successful completion of the project will contribute to the DA and DoD goal of a significant reduction in hazardous waste generation within the 1995-97 timeframe.

The technical approach would be to evaluate this process by a comprehensive characterization of candidate non-chromate conversion coatings/industrial sources and in-house development for Aluminum alloys 2024, 5052, 5083, 5086, 6061, 7075 (with special emphasis on the 5000 series used primarily in combat and tactical vehicles), for comparison with the currently used alodine chromate conversion coatings. Test protocol includes Auger, ESCA and IR spectroscopy analyses, salt fog, Electrochemical Impedance Spectroscopy, adhesion, stress corrosion cracking, outdoor exposure and field tests.

Several sources of supply for the non-chrome sealer will be identified and evaluated in the laboratory with respect to corrosion resistance, abrasion resistance, adhesion, fatigue life. Comparable tests will be conducted in the actual production environment to demonstrate performance equivalent to chromium sealers

#### **Expected Payoff:**

Potential users include MSCs, RDECs, Depots, DoD industrial base. The P.I. of the project is a member of the Aerospace Chrome Elimination Group comprised of the Army, Navy, Air Force, and industry participants (Boeing, Grumman, McDonnell Douglas, Northrop, Rockwell, Lockheed, and Hughes). Use of the non-chromate conversion coating will allow government and industry facilities to eliminate one source of hazardous waste with concomitant cost savings associated with reduction of waste treatment and disposal costs. In 1991, the Army's cost of safe handling and disposal of hazardous waste was estimated to be \$335M. The same cost was projected to be \$75B throughout the industrial base.

#### **Milestones:**

Laboratory Evaluation of Sanchem, Turcoat, Hughes processes, and in-house developed rare earth coating; FY93

Outdoor exposure tests, field tests; FY94

Specification, transition to users; FY95

#### **Transition Plan:**

Coordination with MSCs, RDECs, Depots through membership in Corrosion Prevention Advisory Teams (CPATS) and the Aerospace Chrome Elimination (ACE) Group. Introduce specification for non-chromate conversion coating for aluminum alloys early in the acquisition cycle of a weapon system, and insure flow-down to contractors, sub-tier suppliers and vendors.

#### **Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
NC Conv Coat	150	150
NC Sealer	95	150
Total:	245	300

#### **Performers:**

Department of the Army, Army Research Laboratory (formerly MTL) Materials Directorate, Watertown, MA. Member of the ACE Group, Cooperative development agreements with DoD and industrial base.

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**SERDP Thrust Area:** Pollution Prevention

**Title:** Accelerated Testing Techniques for Environmentally Acceptable Materials and Processes

**Problem Statement:**

The goal of this project is to develop low risk, fast track methodologies and techniques for military qualification of new or modified environmentally benign materials.

Continuing efforts to develop environmentally acceptable materials and processes are constrained by the time-consuming process of qualification testing. Users (customers) must make their decision under conditions of uncertainty and want to take as low as risk possible in the decision. Frequently, substantial testing was conducted in support of the initial product qualification decision or in support of re-qualification for design modification to improve performance or solve problems. The present qualification test process is both time consuming and costly and is often preempted by environmental compliance or enforcement requirements.

There is a real need to develop accelerated and less costly means for qualification testing of alternate, substitute and emerging new materials and processes in order to rapidly introduce environmentally acceptable materials into the military inventory and force structure. Economical means are required in order to preserve a diminishing source base threatened due to costly restrictions.

This is a new project for FY 93 SERDP.

**Project Description:**

The objective of this project is to create combined environmental and reliability test techniques with 20:1 time compression ratio in areas such as corrosion, sonic and low-cycle fatigue, adhesive delamination, canopy deterioration, paint aging, and plastic embrittlement.

An integrated product development (IPD) team will be created to conduct a systems engineering analysis of qualification test requirements and provide focus on where material science and research efforts are required. The IPD team will be composed of representatives of Wright Laboratory Materials Directorate, Flight Dynamics Directorate, Propulsion Directorate, Aeronautical Systems Center Systems Engineering Directorate, Air Logistics Center maintenance engineering, and selected representatives from the material supplier base.

Phase I will identify and prioritize materials and processes requiring costly long lead qualification testing requirements such as corrosion, sonic fatigue, and low cycle fatigue.

Phase II will characterize material aging physics and develop the theoretical bridge between real life testing and accelerated testing on selected characteristics and phenomena.

Phase III will formulate methodologies and present technique design concepts to conduct accelerated testing using advanced techniques, assemble historical life testing results in selected material technology areas, and conduct a limited number of accelerated tests to demonstrate the feasibility and viability of the concepts and correlate results with traditional methods.

There are no known comprehensive efforts accomplished on this specific project. The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort will also enable reduction of risks, costs and liabilities associated with use of toxics, and handling, treatment and disposal of hazardous wastes.

The project will provide a method of accelerating qualification of a large number of technology development projects involving development of alternates and substitutes for materials with hazardous or toxic manufacturing wastes.

The following are tasks associated with the project:

- (1) Select high leverage materials -- those being driven by or forced by legislation
- (2) Characterize time dependent failure modes and test requirements:
- (3) Characterize test modes (fatigue, vibration, corrosion)
- (4) Examine assumptions and rationale behind testing requirements and techniques
- (5) Build theoretical bridge
- (6) Identify most promising acceleration testing methodologies
- (7) Compare and correlate accelerated testing results using traditional materials with those obtained with those using traditional methods (from historical records and qualification test reports)
- (8) Initiate accelerated testing for environmentally benign alternate and substitute materials.
- (9) Link with information sources such as the Government/Industry Data Exchange Program (GIDEP) and the USEPA Pollution Prevention Information Exchange System (PPIES) to exchange qualification test results among programs and assess impacts to military specifications and standards

The major technical issues to overcome relate to acceleration physics; and the degree of empirical evidence required to support configuration change decisions

#### **Expected Payoff:**

Potential users include aerospace manufacturers (especially those manufacturing dual use civilian/military products), Air Logistics Centers, Integrated Weapon System Program Offices, and DoD industrial operations. Professional societies such as American Society for Testing Materials (ASTM) will be invited to participate in reviewing project plans, progress, and results.

The development of an acceptable accelerated testing technology will reduce time for testing, reduce testing cost of testing, and eliminate costs of environmental compliance and hazardous materials/waste management. These efficiencies and economies will result from elimination of unnecessary or redundant tests and earlier implementation of clean technology.



**Milestones:**

Initiate Project	FY 93 Mar
Begin studies to select target materials and testing requirements.	
Target materials and tests isolated	Jun
Contract award	Aug
Initiate studies of failure modes and test modes.	
Failure modes identified	Sep
Test modes identified	
	FY 94 Mar
Aging physics identified	
Theoretical bridge established	May
Peer review	Jun
Advanced testing techniques selected	Aug
Initiate ATTD/Manufacturing Technology planning as required	Dec
	FY 95 Aug
Demonstration of advanced techniques and correlation of test results with historic data	
Technology transfer media released	Sep

**Transition Plan:**

Users will be participants on the IPD team for needs validation, priority setting, methodology approval, and review of demonstration results.

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
100	250

**Performers:**

The project will be performed under the technical leadership and direction of the following:  
Air Force Material Command  
Aeronautical Systems Center  
Wright Laboratory  
Materials Directorate  
Wright-Patterson AFB, OH 45433

The Materials Directorate will award one or more research contracts to industry to perform the development and integration.

To facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans on having the demonstration site to be either an Air Force Material Command Air Logistics Center or the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB Ohio.

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## **SERDP Thrust Area: Pollution Prevention**

**Title:** Non-Hazardous, Low VOC Corrosion Protection Paints and Coatings

### **Problem Statement:**

Paints and coatings applied on board ships in the past contained lead and chromium levels that pose potential health and safety issues to ship personnel during removal operations, as determined by the Navy Environmental Health Center. NAVSEA has since minimized the levels of such hazardous ingredients in paints but has determined the need for further reductions beyond what has been accomplished to ensure ships force health and safety. New Federal legislation regarding acceptable levels of lead and chromium in industrial paints (including marine coatings) will impact current Navy paint and coatings systems.

Navy shipboard applied paints and coatings are currently in a Class I compliance deficiency with regard to some local, state, and federal air pollution regulations pertaining to VOC emissions. This compliance efficiency impacts Navy Fleet preservation and maintenance. Current pending EPA Control Techniques Guidelines (CTG), National Emission Standard for Hazardous Air Pollutants (NESHAP), and subsequent State Implementation Plans (SIPS) will also impact current Navy paint and coatings systems.

The reformulation, testing, and qualification of Navy-specified paints is critical in order to address potential health, safety, and disposal problems associated with the hazardous ingredients in Navy paints, as well as compliance to all Marine coating regulations. In addition, it is paramount to ensuring equal or improved service life performance. This process requires an average of 3 years to complete (in addition to 6-9 months for procurement and supply), underscoring the need for timely funding. Several SEA 08 utilized paints (critical nuclear space application) have no lead-free (<0.06 percent lead by weight) or VOC compliant alternatives.

### **Project Description:**

The technical objective of this program is to reformulate Navy shipboard paints to eliminate hazardous materials (i.e., lead, chromium, etc.) and to conform to Federal and State regulations limiting emissions of volatile organic compounds (VOC). NAVSEA 05M is designated by CNO as the lead for Navy/DoD Marine Coatings Hazardous Materials Elimination and is responsible for addressing these critical fleet issues.

Navy shipboard paints and coatings will be reformulated to meet new stringent limits for hazardous materials and reductions in marine coating VOC regulations. Once completed, the new compliant paints must be tested in the laboratory to ensure that all requirements outlined in the corresponding specification have been met. The paint must then be tested aboard ship to ensure that its in-situ performance is equal to or an improvement of the current paint system. Having successfully completed all testing necessary for qualification, related documentation will be finalized, issued, and procured to. Navy shipboard paints and coatings have in-service performance requirements based upon maintenance schedules and critical need for operational readiness that makes them unique to other DoD/DOE paints and coatings.

**Expected Payoff:**

Navy proactive efforts will ensure the service life performance of Navy paints, reduce hazardous materials and VOC content in paints, and will enable the Navy to transition over to nonhazardous paint in a more timely manner. Thus, more qualified vendors with compliant paint will improve competitive pricing, improve supply logistics for fleet needs, ensure compliance, and avoid costly fines and potential stop work orders. Eliminating hazardous materials from the remainder of paints not yet reformulated will improve worker safety during paint removal operations, decrease the cost of those operations and disposal of removed paint debris.

**Milestones:**

The milestone summary below provides a general description of the specific compliance efforts to be accomplished.

Identify all paints containing lead and chromium ingredients, as well as those paints exceeding new emergent VOC content requirements. Approximately 120 paints are affected.

Determine extent and nature of R&D effort necessary to correct specifications, NAVSEA engineering drawings, manuals, etc., to remove hazardous ingredients and substitute nonhazardous alternatives.

Begin development program to reformulate lead, chromate, and VOC contents in shipboard paints to the lowest content achievable, and conduct necessary testing to validate alternative coatings for specified uses. Program will start on paints known to be lead, chromium, and VOC problems.

Conduct program to develop safety procedures and documentation for fleet use during removal of lead and chromate paints to control worker exposure, dust spread to non-target ship spaces, and removal cost.

Develop new documentation, implementation documentation, and logistics support.

Sub-Tasks under this program include the following:

Lead and Chromium Abatement in Shipboard Paints and Coatings.

Lead and Chromium Containing Paint Removal Technology.

Lead Abatement of Navy Critical Application Paints:

Navy Low Activation Paints (Nuclear Applications).

Water-based Coating Technology (Full Shipboard Implementation).

Reformulation of Marine Coatings to Address Low VOC (275g/L) Limit.

VOC Compliant Alternatives For Low Activation Interior Coatings (SEA 08 - Nuclear Space Applications)

New Transfer Efficient for Low VOC, High Solids Paints.

**Transition Plan:**

NAVSEA has been assigned the lead to transition low lead, VOC, and nonchromium paints and coatings to the fleet. This will be accomplished in the order of criticality of compliance and mission operations. There will be a significant amount of coordination between NAVSEA and GSA to resolve procurement issues associated with new paints, NAVSEA and NAVSUP to resolve stocking and supply issues during the transition of old to new paints, and NAVSEA and the fleet to provide guidance and support in the development and implementation of new paints.

**Funding: (\$K)**

FY93	FY94
3500	4850

**Performers:**

The program director is NAVSEA 05M1. Engineering field support will be provided by NSWC, Carderrock Division, Philadelphia, Detach. and Puget Sound Naval Shipyard. Industry participants include Ocean City Research Corp., Protective Coatings Tech.

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\* Note: The SERDP Scientific Advisory Board provided specific guidance to this project. Their position statement on this effort may be found in a separate section within this document; see "Table of Contents."

## **SERDP Thrust Area: Pollution Prevention**

### **Title: Innovative Very Low VOC Antifouling Paints and Processes**

#### **Problem Statement:**

The Navy needs antifouling coatings that will comply with anticipated changes in volatile organic content (VOC) air quality and current hazardous air pollutant (HAP) laws. Until the mid 1980's, the Navy relied exclusively on MIL-P-15931, Formulas 121 and 129, copper oxide toxic antifouling paints to prevent biological fouling of ship hulls. MIL-P-15931 antifouling coating has an average service life of 18 months. In the mid 1980's, the Navy attempted to institute the use of the much more effective organotin based antifouling paints. However, a combination of State concerns about adverse environmental impacts, issuance of state water quality standards for organotin as low as 1 part per trillion and shipyard worker concerns about personal safety during application and removal prevented the adoption of these coatings.

In the late 1980's, as an alternative to the ablative organotin antifouling paints, the Navy began experimenting with commercial self polishing (ablative), copper oxide based antifouling paints. The experiment was successful and by 1990, the Navy instituted full scale use of these ablative copper oxide antifouling coatings. Currently over 170 ships are coated with ablative, copper oxide based antifouling paints. With minimal underwater hull cleaning, the use of ablative copper oxide antifouling coating has enabled ships to extend fouling free hull service periods from the average of 18 months to over seven years. The current technology antifouling paints, both MIL-P-15931 and commercial ablative coatings meet the existing 400 grams per liter VOC air quality laws, but will not meet the lower VOC regulations anticipated in the future. In addition, HAP requirements require reformulation and retreating of the currently approved antifouling paints.

#### **Project Description:**

The technical objective of this program is to develop and/or demonstrate ablative, copper oxide based, very low VOC antifouling coatings that will meet all future air quality (VOC and HAP) regulations. The program will concentrate two main tasks as well as laboratory testing.

The first task is to evaluate the potential of the Marine Environmental Research, Inc. (MER) concept that combines the use of a waterbase or very low level VOC zinc rich hull coating with a positive potential electrical field impressed on the ship hull. The concept involves using the electrical field to cause controlled wastage of the zinc rich coating causing any fouling present to be sloughed and/or washed off.

Secondly, emphasis will be directed at the development of high solids, waterbase and/or non-HAP, very low level volatile content antifouling paint or processes and the equipment necessary to implement their use in the field. Equipment to be evaluated will include the Uni-Carb CO<sub>2</sub> process.

After successfully passing laboratory tests, the program will progress to demonstration of the coatings and equipment at a shipyard during application of test patches to active ships. The service life and cost effectiveness will be determined.

#### **Expected Payoff:**

A successful waterbased, very low VOC, HAP complying paint or MER type process will guarantee future availability of antifouling protection to the Fleet. Antifouling protection effective and durable for 5-7 years will require less power (less drag) and produce higher speeds for the same power. The antifouling protection also reduces the need for underwater hull cleanings (\$2.4M/yr), reduces the need for scheduled drydocks (\$80M/yr) and minimizes hazardous waste from paint removal (\$2-5M/yr) for an estimated annual total Fleet cost avoidance of \$200M/yr. In addition to reduced costs, effective and durable antifouling protection improves sonar performance by reducing flow noise and contributes to increased ship availability.

#### **Milestones:**

The planned milestones for the Low VOC antifouling paint and processes program are as follows:

FY-93 - Initiate laboratory development and evaluation programs for tasks 1-3 by contract. Testing will be in accordance with MIL-P-24647. Solicit RFPs via Broad Agency Announcement (BAA) in the Commerce Business Daily (CBD). Evaluate responses and award contract(s).

FY-94 - Complete laboratory development and test phase. Begin MIL-P-24647B panel immersion tests. Conduct physical testing of best selected formulations to requirements of MIL-P-24647B. Begin equipment evaluation for MER and high solid spraying. Initiate small scale ship keel panel or patch of best formulation and MER.

FY-95 - Using immersion, small scale ship and laboratory test derived data, fine tune best formulation(s). Complete laboratory and MIL-P-24647B panel/physical testing. Monitor small scale ship testing. Initiate MIL-P-24647B ship patch tests.

FY-96 - Complete all laboratory and small scale ship testing. Monitor ship patch tests. Initiate full scale ship test(s). Prepare draft logistics documents. Recommend for transition.

#### **Transition Plan:**

Products of this project will transition to the Energy R&D Program (PE 63724N/PE 64710N) managed by ONR 12E and/or the Environmental Protection Program (PE 63721N) managed by NAVSEA 05R. Both programs are sponsored by OP-N4 and will monitor coating performance, application and introduction into the Fleet. The estimated R&D costs for this will be \$1M over a 3-year period. The upgrade of the necessary documentation for fleet implementation to achieve significant extension of service life of Navy ships with minimal environmental impact and minimal hull husbandry will be included. NAVSEA 05T program for improved surface ship signature control will monitor compatibility of the new paints with

special substrates. Coatings validated under this project will be applicable to all ship and submarine classes. This project will provide the necessary incentive and introductory technology briefings to the commercial sector in order to establish industrial preparedness for coating production.

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
570	625

**Performers:**

Program Director: NAVSEA 05M1  
Engineering Field Support: NSWC, Carderock Division, NCOOSC, NRL

Industry participants: To be determined by competitive contract award.

**Technical Points of Contact:**

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**SERDP Thrust Area: Pollution Prevention**

**Title: Large Area Powder Coating**

**Problem Statement:**

The goal of the proposed project is to develop and implement surface coating technologies for aerospace systems use which do not require spray application or use of toxics such as volatile organic compounds (VOCs) or isocyanates.

Existing primers and topcoats are solvent based systems that must be sprayed on components to be protected from corrosion or other operating environment conditions. Industrial use of solvent based technology has numerous drawbacks: evaporation of toxic volatile organic compounds (VOCs), release of toxic isocyanates, low transfer efficiency, and relatively long cure times. An alternative technology, use of powder coatings has generated considerable interest within the aerospace industrial community. Powder coating typically involves electrostatic application of powdered metal to a grounded part, followed by a curing cycle to flow the material into a continuous coating. Advantages of powder metal technology include: reduction of toxics use and generation, increased transfer efficiency, and reduced costs of environmental safety and compliance and energy use. Current technology has limitations, however, in use of powder for large parts, such as those on the outer moldline of aircraft. Technology development is needed to obtain the full benefit of powder coatings use in this area of aerospace manufacturing.

This is a new project for FY93 SERDP.

**Project Description:**

Technology for large area powder coating must be developed, optimized, reduced to practice, and qualified for use on Air Force systems.

This program is an integrated program to develop alternatives to solvent based coating systems for large aircraft parts. Considerations in identifying an acceptable technology will include: maintenance or improvement of substrate integrity, effects of part geometries, process quality assurance, and curing specifications. Candidate technologies, including both government and industry initiatives, will be identified and assessed. Development needs will be identified and implemented. Most promising technologies will be developed, optimized, scaled-up, demonstrated and qualified. Needs of Air Logistics Centers (ALCs) and Government-Owned, Contractor-Operated (GOCO) facilities will be given priority attention.

Process studies will be conducted to identify and assess candidate technologies, including both government and industry initiatives. Studies of development needs will be identified and implemented. The most promising candidate technology will be selected for testing, analysis, development, optimization, scale up, demonstration and qualification. Life cycle cost studies will be performed. Prototype will be transitioned to users for extended production evaluation. Needs ALCs and GOCOs will be given priority attention.

The planned effort will be coordinated with Wright Laboratory continuing work on advanced low VOC and powder coating programs.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort will also enable reduction of risks, compliance costs and liabilities associated with use and release of toxics to the environment.

The proposed effort is relevant to various Air Force and industry efforts to develop powder metal technologies for aerospace use. The needs of ALCs are sufficiently urgent to warrant Wright Laboratory participation in the quest for acceptable large area powder coating technology.

Major technical issues include: powder formulation, powder handling and storage, meeting low temperature flexibility and reverse impact requirements, maintenance of proper coating quality and thickness, and curing optimization.

#### **Expected Payoff:**

Availability of acceptable large area powder coating technology will liberate Air Force and industry users from the burdens of using a technology dependent on VOCs and air toxics. The total cost avoidance will be dependent upon the specific applications and the technologies developed. While direct labor, material, and equipment costs may increase, the burdens of environmental compliance and costs of hazardous materials and waste management and response will be entirely eliminated.

The planned effort will not adversely impact system efficiency, capability, or schedule. Experience with detail part technologies suggests that costs may be lower.

#### **Milestones:**

FY93

- |     |   |
|-----|---|
| JUL | <ul style="list-style-type: none"><li>• Initiate project.</li><li>• Initiate studies to define powder coating process mechanisms and requirements for large area coating. Select demonstration site and mobilize R&amp;D team. Design and initiate tests and experiments to determine materials properties.</li></ul> |
| JAN | <ul style="list-style-type: none"><li>• Complete definition studies. Initiate selection of parts and processes to be targeted for development and application of the new technology. Initiate preparation of experimental design for initial technology demonstration.</li></ul>                                      |
| MAR | <ul style="list-style-type: none"><li>• Finalize deposition technology demonstration agenda. Select site for deposition demonstration. Initiate preparations for technology demonstration.</li></ul>  |
| SEP | <ul style="list-style-type: none"><li>• Conduct deposition technology demonstration. Initiate analysis of results in concert with research partners and user technical representatives.</li></ul>   |

FY94

NOV

- Complete review of technology demonstration results
- Initiate validation and optimization studies
- Initiate experiments to determine effects of processes on substrates/parts
- Evaluate process quality and consistency

SEP

- Complete validation and optimization studies
- Initiate planning for scale-up studies
- Determine full scale process requirements in terms of equipment, personnel, sitting, and operating processes.

FY95

NOV

- Complete scale-up planning
- Initiate acquisition and positioning of scale-up elements

AUG

- Conduct pilot scale demonstration
- Review results and determine if full scale is appropriate

#### **Transition Plan:**

Following decision to perform full scale demonstration, a demonstration plan will be developed in concert with the user for the selected demonstration site (ALC or GOCO). Performance testing parameters will be developed, equipment and materials procured and positioned, and staffing and support arranged. Full scale demonstration will then be conducted. Findings will be compiled and made available to prospective users for review and evaluation. After evaluation and acceptance, specifications and standards will be prepared or revised to make the new technology available for production or logistics use.

#### **Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
100	300

Degree of coordination conducted between performer and user: Potential users will be an integral part of the R&D effort for its duration. Their participation and technical inputs will be utilized throughout the technology development and validation process.

**Performers:**

The project will be performed under the technical leadership and direction of the following:

Air Force Material Command  
Aeronautical Systems Center  
Wright Laboratory  
Materials Directorate  
Wright-Patterson AFB, OH 45433

The Materials Directorate will award one or more research contracts to industry to perform the development and integration tasks.

In order to facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans on having the pilot and full demonstration site to be either an Air Force Material Command Air Logistics Center, the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB Ohio, or a selected Air Force GOCO facility.

**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Organic Protective Coatings and Application Technology**

#### **Problem Statement:**

To develop high performance, non-toxic, low volatile organic compounds (VOC) content coatings for Navy use. Organic coatings are the primary source of protection against environmental degradation for Navy aircraft (A/C), weapon systems and ground support equipment (GSE). In addition, these materials provide passive countermeasures against many enemy threats. There are a large number of different coating systems currently used by the Navy due to the diverse nature of their functions; the variety of substrates & alloys to which they are applied; and the severe nature of their operational environment. These protective coatings contain toxic inhibitors (i.e., lead, chromates, etc.) and high VOC contents. These components are released during painting operations as organic and toxic air emissions. Federal, state and local environmental agencies like the EPA and California Air Quality Management Districts (AQMD) classify these materials as hazardous and restrict their emissions through regulations such as the Clean Air Act, Clean Water Act, CERCLA, Resource Conservation and Recovery Act (RCRA) as well as local EPA and AQMD rules. In addition, OPNAVINST and CNO directives require significant reductions in hazardous waste generated by the Navy. Finally, painting operations at maintenance depots are a major contributor to hazardous material and waste generation in the DoD. Therefore, it is necessary to develop new high performance coatings that meet current and future environmental restrictions while allowing the Navy to continue painting operations.

#### **Project Description:**

A full spectrum approach for reducing the VOC and air toxic emissions from protective coatings will be pursued. To begin with, research in low VOC polymer technology will be used to produce low VOC binder systems. Reactive monomers/oligomers and diluents will be developed to obtain low viscosity, low VOC binder systems for future organic coatings. In addition, recent developments in water-borne resin technology by coatings manufacturers will allow for the development of high performance water-borne topcoats which are compliant with these regulations. Coating corrosion resistance, physical performance properties and VOC content will be evaluated to develop the best materials. Furthermore, low/no VOC protective coatings (such as electrocoatings, powder coatings, bearing adhesives, fuel cell repair, and NDI penetrants) will be investigated for potential aerospace applications.

Several recently developed VOC compliant, non-toxic alternative materials will be investigated for this program. These compliant coating systems include Unicoat (a non-lead, non-chromate, low VOC self-priming topcoat); compliant lacquer topcoats and non-toxic inhibitor systems. The non-toxic inhibitor systems will be used to develop replacements for the current lead and chromate containing materials. These materials will be optimized, service evaluated and implemented for Navy use. Finally, conventional air spray used to apply these materials, has a transfer efficiency of only about 28 percent. Therefore, investigating high-transfer efficient spray application equipment would significantly reduce the amount of air emissions from painting operations. Application equipment such as

air-assisted airless, electrostatic, high volume low pressure (HVLP), and plural component will be evaluated.

### **Expected Payoff:**

The development of non-toxic, VOC compliant coatings will enable the Navy to meet current and future environmental regulations as well as reduce the total amount of hazardous waste the Navy generates. In addition, these new materials will eliminate the need for the installation of extremely expensive control equipment (i.e., \$1-5M per spray booth for VOC emission control). This effort is in direct support of Navy and DoD hazardous waste minimization policies/directives. In addition to reduced handling and disposal costs, Navy A/C and equipment operational readiness will be maintained by using these new coatings. This is particularly important considering the cost of these A/C, weapon systems and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also be transition to many areas of the commercial sector (aerospace, automotive, marine, etc).

### **Milestones:**

Implement Unicoat—Self-Priming Topcoat	FY93
Service Demonstration of Compliant Lacquer Topcoats	
Optimize Non-Toxic Inhibited Organic Coatings	
Optimize High Transfer Efficiency Application Equipment	
Develop Water-Borne Topcoats	
Develop Low VOC Polymers for A/C Coatings	
Implement Compliant Lacquer Topcoats	FY94
Service Demo of Non-Toxic Inhibited Organic Coatings	
Implement High Transfer Efficiency Application Equipment	
Optimize Water-Borne Topcoats	
Develop A/C Coatings Based on Low VOC Polymers	
Investigate Compliant NDI Penetrants	
Implement Non-Toxic Inhibited Organic Coatings	FY95
Optimize Low VOC Polymer Coatings	
Service Demonstration of Optimum Water-Borne Coatings	
Develop Powder Coatings for A/C Applications	
Develop Electrocoatings for A/C Applications	
Develop Supercritical CO <sub>2</sub> as a Coating Diluent	
Optimize Compliant NDI Penetrants	
Implement Water-Borne Topcoats	FY96
Service Demo of Optimized Low VOC Polymer Coatings	
Optimize Powder Coatings for A/C Applications	
Optimize Electrocoatings for A/C Applications	
Optimize Supercritical CO <sub>2</sub> as a Coating Diluent	
Initiate Non-VOC Fuel Cell Repair	
Initiate Non-VOC Bearing Adhesives	

**Transition Plan:**

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP and transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination throughout the development and evaluation of these materials/processes will ensure availability for implementation.

**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
Y817	60	
SERDP	490	430

**Performers:**

Development of non-toxic, low VOC protective coatings is being performed by the Naval Air Warfare Center Aircraft Division Warminster, Naval Aviation Depots and the Maintenance Technology Center for Environment. These efforts are being coordinated with resin/coatings industry, Air Force (Tinker AFB, Kelly AFB and Tyndall AFB), Army and aerospace industry (MCAIR, Boeing, etc.).

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## **SERDP Thrust Area: Pollution Prevention**

**Title:** Investigate Water-Based Coating Systems for Military Clothing and Equipment Items

### **Problem Statement:**

The Army has adopted a pollution prevention hierarchy which has source reduction/material substitution as the most desirable approach to minimizing hazardous waste generation. This project focuses upon reducing hazardous waste by investigating commercial fabric coatings applied through non-solvent processes for potential applications on military clothing and equipment. This project will improve the Army's image with regard to protecting the environment and establish the Army as a leader among the military services in the environmental safety arena. The project would also yield coated fabric products meeting the needs of the soldier while promoting a more competitive commercial supply base.

### **Project Description:**

The technical approach can be described as follows: the initial project step is to conduct a market survey to identify likely candidate coatings. Develop samples in military coated fabric configurations for test and evaluation. Develop recommendations for further, expanded production trials and field evaluations of promising coating concepts. Subsequent project steps include conducting expanded production trials, fabricating test garments and conducting field wear study of candidate coated fabrics in test garment form. Upgrade Technical Data Packages with acceptable coating alternatives.

### **Expected Payoff:**

It is expected that this project will demonstrate that they are viable nonsolvent coatings options for military unique clothing. The results will allow the Army, and potentially all services, to use reduced hazardous chemicals in the manufacture of clothing.

### **Milestones:**

The tasks/milestones are shown below for the life of the project:

Conduct market survey and initial material tests	FY93-94
Concept production scale-up and Technical Test	FY95

### **Transition Plan:**

The technology developed and proven in this project will be made known through bulletins, reports, and articles for leading clothing manufacturers. This project's results will be made available especially to those Navy, Marine Corps, and Air Force clothing specialists who would be able to adapt the project results to their Department's needs.



**Funding: (\$K)**

The total funding from SERDP to complete this demonstration project is \$490,000. Below, this figure is separated by fiscal year, by total, and by in-house government personnel.

	<b>FY93</b>	<b>FY94</b>
SERDP	130	180
Service Funds	50	80

**Performer:**

US Army  
Individual Protection Directorate  
Textile Research and Engineering Division  
Natick Research Development & Engineering Center  
Natick, MA

**Technical Point of Contact:**

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**SERDP Thrust Area: Pollution Prevention**

**Title:** Nonvolatile Organic Compound Chemical Agent Resistant Coating

**Problem Statement:**

Federal and local regulations resulting from the Clean Air Act restrict the amount of volatile Organic Compounds (VOC) emitted during the application of protective coatings. There will be lower VOC limits in the future, and several localities already have limits lower than required by the EPA. The goal of this project is to develop a water reducible/water dispersible (WR/WD) Chemical Agent Resistant coating (CARC) for use on Army Tactical Vehicles. CARC is mandated on all combat, combat support, and essential ground support equipment, plus tactical wheeled vehicles and aircraft.

Proposed technology customers include all users of CARC on tactical equipment, including depot activities in the Army, Navy, Air Force, and Marine Corps. This project represents a new start.

**Project Description:**

The investigation will focus on use of high performance, WR/WD polyurethane binder systems which have the potential for chemical agent resistance. Requirements to be addressed by this project for the WR/WD CARC will include compatibility with current camouflage pattern painting procedures and universal use under all current and foreseen VOC regulations.

**Expected Payoff:**

Development of a more environmentally acceptable CARC will lead to lower VOC emissions and consequently reduced photochemical smog formation. In addition, worker exposure to potentially hazardous solvents is minimized. Finally, in localities where VOC regulations are more stringent than the current federal limits, Notices of Violation (NOV) will be averted.

**Milestones:**

	Completion Dates
Survey of technology and sample acquisition	6 months (FY93)
Screen candidate polymers for agent resistance	12 months (FY93)
Optimize camouflage pigmentation	18 months (FY94)
Develop and publish a material specification	24 months (FY94)

**Transition Plan:**

Via a material specification

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
150	150
150	150

**Performer:**

Same as the Technical Point of Contact. The managing organizations are ARL and AMSRL-MA-E.

**Technical Point of Contact:**

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**SERDP Thrust Area:** Pollution Prevention

**Title:** Flame Spray of Thermal Plastic Coatings

**Problem Statement:**

Current protective coatings require harmful solvents for proper application. Objective is to apply the technology of flame spray to eliminate solvents.

**Project Description:**

This program would reduce the amount of harmful solvents released into the atmosphere in addition to creating a healthier environment for the workers applying the coating. A commercially available flame sprayer utilizes powdered thermoplastics which can be applied to almost any surface. This technique has been demonstrated on composite parts and should be applicable to other materials as well. Parts would be sprayed and then compared to parts coated using traditional methods. Testing will be done for thermal cycling and compatibility with chemical agent removal systems. Complete environmental test cycles will be completed.

**Milestones:**

Composite tubes have been sprayed and the equipment is available to coat almost any shape or size part. Facilities are available to complete test cycles.

Effort will involve identifying potential spray materials. These materials will then be sprayed on various substrates for initial proof of concept. FY93

Materials on substrates will be tested for thermal cycling, heat absorption, IR signature, and reflectivity. There will also be a compatibility test with chemical agent removal systems. FY94

Implementation of process and materials using actual ordnance. FY95

**Funding:** (\$K)

	<b>FY93</b>	<b>FY94</b>
SERDP	100	100
Service Funds	85	85

**Performers:**

Composite Structures/Materials Function, Structures Directorate, RD&EC, USAMICOM

**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

**Title:** Joint DoD/DOE Program for Agile, Clean Manufacturing Technology for Propellants, Explosives, and Pyrotechnics (PEP)

### **Problem Statement:**

Propellants, explosives, and pyrotechnics (PEP) used by Defense are required to reduce their hazardous wastes by at least 50 percent by 1997. Energy and NASA also have PEP waste reduction requirements. Past waste reduction was accomplished by cleaning up PEP production processes. Future waste reduction can be achieved by reducing wastes throughout the PEP product life cycle. The product life cycle includes synthesis of PEP chemicals; formulation of chemicals into a product; chemical processing, loading, and unloading of the product; combustion emissions; and methods to reclaim, recover, and recycle excess material.

The goal of the program is to develop integrated product/process development (IPPD) technologies and tools to achieve a design for reconfiguring existing PEP production facilities into agile factories which will reduce total life cycle wastes by over 90 percent from the 1992 PEP waste baseline. In the context of this proposal, a factory is defined to be the set of existing, geographically separate, PEP facilities that produce PEP products, recycle the production by-products into usable products, or recycle PEP parts returned as excess from the ordnance inventory.

Approximately 500 million pounds of PEP are produced each year for DoD, DOE, and NASA as main charge explosives, solid rocket propellants, and flares/illuminators. PEP chemicals and products are produced in government operated, GOCO, and defense contractor facilities. Ever stricter environmental regulations and waste restrictions are forcing some PEP chemicals from the ordnance inventory (most notably TNT). Today waste generating PEP components are approved for inclusion in new products through a waiver process that allows polluting PEP products into new ordnance. As public concern about waste generation increases, these waivers will become increasingly difficult to obtain.

Significant advances have been made synthesizing new PEP chemicals (e.g., ADN, CL-20, NTO, TNAZ). These new chemicals could enable significantly lower pollution PEP products. Since factories that produce and handle these new materials have not yet been designed and built, they are prime candidates for demonstration of the TPPD approach that will enable design of the clean, agile factories that will be able to comply with future environmental regulations.

### **Project Description:**

The technical objective is to develop critical pollution prevention technologies and an IPPD based factory design that will enable greater than 90 percent reduction in total PEP life cycle wastes compared to the 1992 baseline.

The technical approach is for governmental and industrial PEP R&D labs, pilot plants, and production facilities to be organized into a program network. Present products, processes,

PEP chemicals, and technologies will be surveyed. Models and simulations will predict life cycle performance. Pollution prevention technologies and new factory concepts will be experimentally tested in existing facilities. When use of existing facilities is not practical, a special demonstration testbed may be built. The factory design will then be developed, including detailed descriptions of products, chemical engineering unit operations, utility requirements, regulatory and qualification approaches, safety, and pollution prevention devices to be used in its operation.

The task of accomplishing product and process requirements will be to gather and analyze information in order to form the basis for establishing the characteristics of the life cycle pollution prevention process. A government and commercial user survey will establish a data base of:

- (1) desired product and process characteristics,
- (2) products and processes in use and in development,
- (3) collateral products, e.g., chemicals produced from by-products,
- (4) potential markets for the military and non-military products.

Experimental studies will be conducted by evaluating a range of products and processes as they are utilized in program network laboratories and pilot plant experiments. These experiments will demonstrate new PEP chemicals, products, and processes that are practical for safe, cost-effective, environmentally clean implementation during the PEP life cycle, and satisfy ordnance performance requirements. The successful demonstrations will define the chemical engineering unit operations for the agile factory design. Pollution prevention demonstration subtasks would include:

- (1) reformulating PEP to have clean combustion emissions,
- (2) producing PEP chemicals (crystalline explosives, energetic polymers, plasticizers, oxidizers) in environmentally clean processes,
- (3) manufacturing PEP in a solventless operation, or using environmentally acceptable reagents and solvents,
- (4) evaluating reclamation strategies for recycling and reusing excess PEP from production waste streams,
- (5) decomposing PEP into commercial materials, such as fertilizer, or into innocuous products such as water,
- (6) demonstrating environmental improvements to meet current and future regulations,
- (7) demonstrating PEP products meeting ordnance designer life cycle safety, performance, and environmental requirements.

The program network members will evaluate the state of modeling and simulation in order to determine possible needs for: a standardized process description language, cost models, or models of detailed chemical processes. A Process Modeling System enterprise simulation framework will be used to organize the PEP models. The simulation will test a variety of factory concepts. It will also be used to integrate the complete pollution picture for the PEP product life cycle. A model for minimizing life cycle pollutants will be developed. Models and simulations will be validated by the experiments.

Factory design is also an important task as it is needed to specify the integrated chemical operations for the factory. The data, unit operations, and models developed under the proceeding tasks will provide the tools for the design task. The life cycle pollution prevention demonstrations done by members of the program network in the previous tasks will provide an input/output design for all components, including energy cogeneration using emitted gasses and waste products. Where necessary, the program network team will join with EPA and the explosive safety community to develop experimental regulatory concepts to enhance factory safety, performance, and environmental compatibility. A simulation of the factory structure and physical design will be used to assess trade-offs.

The relationship of this program to the DoD/DOE environmental objective is that this effort directly supports Pillar 3 (Pollution Prevention) of the Tri-Service Users Requirements, items I.6.a-f and I.6.h: Reduction of hazardous waste by 50 percent in ordnance manufacture. The reconfigured factory processing new PEP chemicals should produce significantly less waste than the Pillar 3 objective. It also supports accomplishment of Pillar 3 item III.2.d-f: Methods for developing environmentally sound weapons systems.

The DoD/DOE PEP program relates to ongoing or past work in many ways. As an example, work at the Naval Surface Warfare Center has demonstrated: a solventless cryogenic technique using liquid  $N_2$  in place of conventional solvents to process PEP; use of supercritical fluid extraction techniques to reclaim and reuse PEP returned from the arsenal; and use of PEP wastes to cogenerate heat or electricity. Each is a candidate process for the reconfigured factory.

An ongoing SERDP program at Lawrence Livermore National Laboratory on recycle, reuse, and environmentally safe disposal of explosive waste will assist in identifying recycle product options. Additionally, the Los Alamos National Laboratory Process Modeling System simulation software was developed to aid in the selection of process technologies used in nuclear weapons production. Models for high explosives component manufacturing and weapons assembly/disassembly are being developed.

Another relationship between the DoD/DOE PEP program and ongoing work is that the synthesis of various new energetic ingredients such as: ammonium dinitramide (ADN), nitrotriazolone (NTO), hexanitrohexaazaisowurtzitane (CL-20), energetic polymers with polyether backbones (glycidyl and oxetane backbones), and energetic plasticizers for formulation into advanced energetic formulations. Energetic monomer and polymer scale-up in continuous flow reactors have been initiated at Thiokol and Aerojet. Synthesis of ADN in laboratory facilities is being supported by SDIO, NASA, and ONR at SRI International. An alternate synthesis approach for HMX production was developed by the Army and Lawrence Livermore National Laboratory in the MUSALL project. These new materials and synthesis methods make practical a search for production methods that reduce pollution through the PEP life cycle.

Reclamation of PEP formulations can be done using solvents in the super critical state. ADN offers an unusual reclamation opportunity. ADN is a chlorine free oxidizer which could replace ammonium perchlorate, eliminating the ozone depletion and acid rain Space Shuttle launch issues. ADN decomposes to ammonium nitrate and  $N_2O$  (laughing gas) in an acidic

aqueous environment. This property makes possible the conversion of future ADN based PEP into ammonium nitrate for sale as a commercial fertilizer.

Lastly, the Army Production Base Modernization program directly relates to the DoD/DOE PEP program as it supports development of improved production capability at GOCO factories. They have a demonstration testbed in the design stage, called the Flexible Manufacturing Facility for Energetic Materials, which could be adopted for the mixing, processing, and loading phase of this effort.

#### **Expected Payoff:**

This program will result in a design, by 1997, for reconfiguring existing PEP factories to reduce hazardous wastes by a factor of ten, almost twice the 1997 national goal for pollution prevention. This will preclude price increase of future PEP products due to cost of complying with environmental regulations. Satisfying regulations will preclude factory shutdowns or unscheduled retirement of ordnance systems.

Utilizing the program network of laboratories, pilot plants, and production facilities will:

- (1) preclude duplication of existing facilities,
- (2) reduce construction funds needed for new plants, and
- (3) allow each unit to contribute to the life cycle phase in which it is most knowledgeable.

The models and simulations will provide an understanding of the 1992 baseline, assist in evaluating alternative processes to surpass the national goal, and quantify future environmental gains which might be achieved through agile factory design.

Experience applying IPPD technology to actinide processing in the DOE indicates that dramatic cost reductions can result. DoD facilities might produce PEP products at a commercially competitive cost, making dual use of the factory feasible for commercial explosives manufacturers.

#### **Milestones:**

Technology transition plan & program network established	6 MO
Pollution prevention product/process surveys complete	9 MO
Life cycle simulations of candidate PEP product	12 MO
Formulate target high performance, clean burning propellant	15 MO
Select PEP chemicals to be produced in demonstration	18 MO
Demonstrate solventless/clean solvent & reagent production	24 MO
Complete evaluation of chemical engineering unit operation	30 MO
Simulation & experimental validation of IPPD factory concept	30 MO
Life cycle trade-off analysis complete	36 MO
Environmental regulatory demonstration complete	42 MO



PEP product qualification demonstration complete	45 MO
Complete factory design	45 MO
Estimate factory life cycle wastes relative to 1992	48 MO

#### **Transition Plan:**

The customers are existing production and reclamation factories. Introduction of the new PEP chemicals and processes into the existing factories will achieve the Pillar 3 ordnance DoD/DOE environmental objectives. Customers include the Army Single Manager for ammunition procurement and ammunition production base modernization. The Defense Conversion Armament Retooling and Manufacturing Support Program (ARMS), the NASA propellants production programs, and the DOE's complex reconfiguration program are potential customers.

The enterprise simulation software will be transferred to chemical industries through the Cooperative Research and Development Agreements (CRADA). Standards to support modeling and simulation will be integrated with industry standardization processes.

#### **Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
2000	5000

#### **Performers:**

This program will be managed by a joint DoD/DOE office residing in the DoD. A program advisory panel of government and industry PEP R&D and production managers will be formed. The panel will provide guidance to the program so as to ensure that the program products will transition into the DoD and commercial PEP production bases.

The performers in the program network will include DoD ordnance laboratories (e.g., Naval Surface Warfare Center, Wright Laboratory. Armaments Directorate), DOE National Weapons Laboratories, Army owned GOCO plants (e.g., Holston, Longhorn) and the DOE Pantex production facility. After program initiation, industry R&D labs, pilot plants, and PEP production organizations will be added to the program network.

#### **Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Development of Non-Polluting Primary Explosives**

#### **Problem Statement:**

To develop organic primary explosive compounds that do not contain heavy metal atoms like lead and mercury (as in lead azide, lead styphnate, mercury fulminate and NOL 130) that pose a serious environmental problem when they become waste material. (In general, inert heavy metal compounds, derived from the above explosives when the latter are subjected to hazardous waste chemical treatment, are acutely toxic.) Lead discharges must be abated prior to demilitarization operations. Heavy metal primary explosives are almost always used in fuze trains of munition warheads. In particular, they are present in the detonator assembly which is responsible for the functioning of munition items. Revised EPA regulations make it difficult to destroy obsolete or deteriorated bulk explosive or fuze train components because of the lead content. Costly incineration facilities with state-of-the-art pollution systems must be built which collect the lead, so that it can be ultimately landfilled as hazardous waste.

Lead discharges must be controlled during the production of fuze train components which contain the primary explosives. Waste materials and equipment washdown systems must be segregated and specially treated to prevent lead discharges.

#### **Project Description:**

It is desirable to find organic explosive substitutes which can be incinerated or, perhaps, even degraded enzymatically when they turn into hazardous wastes. They must possess, as a minimum, thermal and chemical stability; a controlled amount of thermal, impact and shock sensitivity and detonation properties that resemble those of the heavy metal primaries. A class of such explosive compounds that is likely to contain the desired substitutes are polynitro alkyl ammonium nitrates. One member of this broad family of compounds, viz. 1,1,1 trinitropropyl ammonium nitrate, is a sensitive and super energetic explosive that was readily synthesized for the first time in the early 1980s for ARDEC's More Powerful Explosives Program.

The explosive was prepared from the basic 1,1,1 trinitropropyl amine by a simple and cheap neutralization reaction with nitric acid. The same type of reaction should produce a great many explosives of this class from a variety of polynitroalkyl amines. It should therefore be possible to synthesize the particular polynitroalkyl ammonium nitrate explosive that most closely resembles the heavy metal primary in the required set of properties. Thus, for example, if 1,1,1 trinitropropyl ammonium nitrate is more sensitive than required, one would attempt to synthesize and test the 1,1,1 trinitrobutyl or 1,1,1 trinitroamyl derivatives of ammonium nitrate or their isomers.

In general, the optimum substitute explosive could be designed for synthesis by adjusting the oxygen balance within the polynitroalkyl group that is, so to speak, grafted on to the stable "ammonium nitrate" trunk of the ionic molecular skeleton. An additional environmental benefit should also accrue from the recent discovery that oxidoreductase enzymes ( in a

polymer matrix) completely convert (ionic) nitrates to environmentally friendly decomposition products like nitrogen.

**Expected Payoff:**

The development of replacements for lead azide, lead styphnate, and/or related formulations (for example, NOL-130 primer mixture) which eliminates lead offers the following benefits:

1. Elimination of lead from the waste stream.
2. Reduce demil/destruction costs.
3. Reduce health hazard to production workers.
4. Potential for reduced cost, improved sensitivity characteristics, improved stability characteristics, improved safety and performance characteristics.

Primary explosives, detonators, initiators, and fuze trains would be the items affected by this project.

**Milestones:**

FY 93-94

1. Custom-synthesize 1,1,1 trinitropropyl ammonium nitrate and conduct stability, sensitivity and performance tests.
2. Design and synthesize additional polynitro alkyl ammonium nitrates.

FY 95-96

1. Conduct stability, sensitivity and performance testing on the most promising polynitroalkyl ammonium nitrates and downselect the organic substitute explosive for the heavy metal primary explosive.
2. Write summary report.

**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
SERDP	267	333
Service Funds	187	233

**Performers:**

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Plutonium and Uranium Metal Forming Technologies**

#### **Problem Statement:**

The goal of the proposed research and development of new metal forming technologies for plutonium and uranium. By reducing the number of processing steps required to manufacture parts, not only is waste generation and cost lowered but also the potential for pollution is reduced. The target of this program is the Department of Energy and its weapon component prototyping and manufacturing facilities. This program addresses the direction given in the enabling legislation (Public Law 101-510) that in § 2902.e.4.B specifies research and development "to minimize waste generation, including reduction at the source". The background to this work is that precision casting technologies exist, such as die casting, that allow net-shape or near-net shape casting. When applied to hazardous materials such as plutonium and uranium, these technologies offer the possibility for significant benefits over the conventional processes of ingot casting, rolling, cutting, forming and machining. This program is an continuation of a previously funded effort.

#### **Project Description:**

A limited amount of work has been performed at Los Alamos and Y-12 to show the feasibility of near-net shape casting of uranium, supported by waste minimization programs. Similar work has been performed at the Rocky Flats plant and at Lawrence Livermore to demonstrated the feasibility of (net-shape) die casting of plutonium. These previous efforts established the technical basis for the previously funded SERDP project with the same title.

The overall objective is to reduce waste generation form the processing of plutonium and uranium, especially mixed wastes. More specifically, the objectives are to increase the current moderate efficiency of the plutonium process to be highly efficient and to raise the current very low efficiency of the uranium process to medium efficiency. These improvements in the primary processes are amplified in the secondary and tertiary waste streams because of the larger volumes of such wastes.

The technical objectives are to apply precision die casting technology to plutonium casting to eliminate essentially all machining and to apply near-net shape casting technology to uranium to eliminate the majority of the forming and machining steps currently used.

The approach that will be used to achieve the objectives of net-shape or near-net shape casting are subtly different for the two materials. For plutonium, precision die casting will be applied to obtain the actual net shape part. S sprue must still be allowed for, however, and this will be removed form the casting by a shearing operation. The whole operation will be enclosed in a glove-box, not only for control of contamination and worker radiation exposure but also for atmosphere control. Plutonium oxidizes very easily and must be processed in a stringently controlled atmosphere in order to minimize waste and to produce acceptable surface finishes in the as-cast part.

For uranium, however, the higher melting point means that net-shape precision casting methods have a much lower probability of success. Therefore the approach is to apply near-net-shape casting techniques with semi-permanent or investment molds. Chill casting, heat treatment and micro-alloying will be investigated for their ability to produce the desired microstructure. Concurrently, advanced modeling techniques for fluid flow, heat flow and thermomechanical behavior will be applied to the developing processes in order to improve our understanding of them and to optimize them.

Examples of the underlying scientific issues are: microstructure control by microalloying; surface treatment of molds to control heat transfer and eliminate metal-mold reactions (which is important for waste control); heat treatment of castings for dimensional control.

The descriptions of the tasks are as follows. For plutonium casting, the task is to replace all the forming steps by a single step die casting process that almost all the waste generating processing steps associated with the conventional process. Although die casting technology is well developed for metals such as zinc and aluminum, the highly reactive nature of plutonium introduces several significant challenges. Mold materials that are resistant to attack and erosion as well as having the correct thermophysical properties, for example, will be developed. The atmosphere in which the processing takes place will be carefully controlled to exclude oxygen in order. A minor machining operation will be developed because it is not possible to make a casting without a sprue.

Uranium has a significantly higher melting point than plutonium (1120°C as opposed to 660°C) and this puts it into the same class as copper in terms of melting point, besides being nearly as reactive as plutonium. One of the main tasks, therefore, is to develop mold materials that are suitable for near-net shape casting. The candidates are graphite, investment molds and metallic mold materials, each of which requires its own development effort. There is a significant degree of common need to mold materials between the two efforts so there will be an active communication between the two development activities, particularly for metal mold materials. Other tasks relate to defining the mold filling process and controlling solidification rate to prevent defect formation. Modeling of fluid flow, including the interaction between heat flow and solidification, is essential to this task and several large scale computer codes (e.g. FLOW3D) are being applied as part of the currently funded effort to carry out this crucial aspect of concurrent engineering.

This proposal addresses the overall DOE environmental objective of reducing the amount of waste of all kinds, especially mixed waste, that is generated during manufacturing of weapons components. As stated in the enabling legislation, this development will address the need to reduce waste generation at its source, and, therefore, the potential for pollution. The components that are the target of this effort are made from hazardous material such as uranium and plutonium as all types of waste, from primary to tertiary waste, has significant impact in terms of cost, radiation exposure to workers, capital cost and size of factory footprint. DoD also uses components manufactured from uranium alloys such as anti-tank penetrators. Success in this area will minimize the potential for pollution from such manufacturing processes for both departments.

The Precision Flexible Manufacturing Systems (PFMS) program at Los Alamos, mentioned above, is related to this proposal because it addresses some of the issues in machining and

inspection that are important to the success of near-net shape casting. A limited amount of work has been performed at Los Alamos and Y-12 to show the feasibility of near-net-shaped casting of uranium, supported by waste minimization programs. Similar work has been performed at the Rocky Flats plant and at Lawrence Livermore to demonstrate the feasibility of die casting of plutonium. These efforts were the basis for a previously funded SERDP project with the same title. The specific milestones that are associated with the previous program are as follows. Please note that these milestones relate to a very recently started effort.

#### Plutonium Die Casting Development

Feasibility Report	Nov. 1992
Reproducibility Test	Feb. 1993
Die Casting Dev. Report	April 1993
Prototype Design	Nov. 1992
Prototype Operational	April 1993
Prototype Operation Report	Aug. 1993
Production Design	Nov. 1993

Process Modeling and Optimization is Concurrent with Milestones

#### Uranium Near-Net-Shape Casting Development

Flat Plate Feasibility	Nov. 1992
Alloy Plate Feasibility	Feb. 1993
Plate Demonstration	June 1993
Hemishell Feasibility	March 1993
Alloy Hemishell Feasibility	Aug. 1993
Hemishell Demonstration	Nov. 1993

Process Modeling and optimization is Concurrent with Milestones

These milestones are associated with a timeline that has only just been activated, however, so it is not possible to report on technical progress for the currently funded program.

The technical risks associated with project are considered to be low as the overall objective is to apply and develop established technologies for hazardous materials. The main risk is that the degree of waste reduction will be less than planned because of unforeseen technical obstacles. The main issues to be overcome are those related to control of casting shape, reproducibility and metallurgical quality. The latter issue arises because of the numerous types of casting defects that can arise and which are discussed elsewhere in the proposal.

#### Expected Payoff:

Nuclear Weapons require the use of highly hazardous materials, notably plutonium and uranium. Both of these materials undergo extensive metallurgical processing in the conventional production process. Plutonium has long been known for its hazardous nature and been handled in a highly controlled manner (gloveboxes, etc.). Therefore the cost and impact of reducing the amount of material sent for recovery is very significant. In addition, reducing the number of processing steps reduces the amount of worker time required to process a part and therefore will lower radiation exposures. The change for uranium is even more striking. Uranium used to be regarded as a heavy metal that happens to be mildly

radioactive. Its radioactivity, however, now means that waste from uranium forming processes is hazardous, adding enormously to the cost of processing the metal and its alloys. Also, the public's desire to minimize the occurrence of contamination of the workplace, workers, or the environment, means that many operations with uranium may have to be performed in enclosures in the future. Therefore the payoff for both plutonium and uranium processing is that successful development of net-shape or near-net-shape casting processes will result in large reductions in waste generation, and thus help to prevent pollution.

The payoff of this program in terms of technology transfer is that process models will be developed in order to be able to optimize the casting processes. These models will address a broad range of phenomena from fluid flow and mold design to residual stresses in parts. These process models are of general applicability to many industrial needs. Another payoff for the technology to be developed in this program is that technologies are being developed for highly reactive metal alloy systems. Thus the special techniques that are developed for near-net-shape casting of reactive metals are expected to be transferable to industrial needs for important industrial materials such as titanium alloys. Titanium is similar to uranium and plutonium in that it is highly reactive so that it must be melted and cast under controlled atmospheres and with special mold materials. For example, standard sand molds are unsuitable for reactive metals such as uranium and titanium which means that there is the same need for special mold materials, e.g. coated refractory metals, in both systems.

#### Milestones:

The milestones proposed for the continuation of plutonium and uranium casting development are intended to allow for a smooth transition from the currently funded effort. Both parts of the program will have significant new content, however. The milestones for plutonium casting relate to continued metal mold and coating development (die lifetime studies), demonstration of the die casting process and the development of methods for sprue removal (that involve some form of machining) and design of a production system. The milestones for uranium casting relate to extending methods developed for simple shapes to the more complex case of cylindrical shapes. In addition to developing techniques for new shapes, development will continue on the flat plate and spherical shells for machining and inspection with a particular emphasis on the development of techniques for locating the final part shape within a narrow envelope. Also, a start will be made on a more complex alloys with higher solute content, for which segregation problems are more significant than the current alloys.

#### Plutonium Die Casting Development

Prototype Process Prove-In (Die Casting)	6 months
Process control definition and Casting Reproducibility	9 months
Development of Special Machining for Sprue Removal	12 months
Design of production system	12 months
Year-end Report	12 months

Process Modeling and Optimization is Concurrent with Milestones

#### Uranium Near-Net Shape Casting Development

<sup>1</sup> Cylindrical Component Feasibility	6 months
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<sup>1</sup> Alloy Cylinder Feasibility	9 months
Cylindrical Component Demonstration	9 months
<sup>2</sup> Alloy Cylinder Demonstration	18 months
<sup>1</sup> High Alloy Plate Feasibility	10 months
Year-end Report	12 months

Process Modeling and Optimization is Concurrent with Milestones

1 These milestones include the evaluation of alternative semi-permanent and permanent mold materials.

2 This milestone depends on continued funding beyond current one year proposal.

Dates for milestones are given in months from receipt of funding although it is expected that the start of the continuation program will coincide with the completion of the currently funded effort.

#### **Transition Plan:**

This program will lead to transfer of the near-net shape forming technology to the appropriate production plant. In the case of uranium, the appropriate plant is the Y-12 plant in Tennessee and this plant is identified as one of the performing agencies for the program. In the case of plutonium it is less clear which the appropriate production plant will be as this may be dependent on the results of the ongoing analysis by DOE Reconfiguration Office of the nuclear weapons complex. The date for initiating any technology transfer will be dependent on technical progress.

Technology transfer from this program is expected to arise from the concurrent engineering component of the program. As the process modeling tools that are developed during the program mature, interactions with industry will be developed with a view towards CRADAs.

#### **Funding: (\$K)**

	<b>FY93</b>
Plutonium Casting	2100
Uranium Casting	2900
Total	5000

The previous funding for this program was 6.1 M\$ from FY91 funds, divided between the plutonium and uranium casting efforts as 2.6 and 3.5 M\$, respectively. The requested funding for this program is 5 M\$ for FY 93, to be distributed between the performing agencies. Los Alamos and Lawrence Livermore will cooperate on the plutonium casting development, whereas all four institutions (LANL, LLNL, Y-12, SNLA) will collaborate on the uranium casting development.



**Performers:**

The performing agencies will be principally the Los Alamos and Lawrence Livermore Laboratories with significant contributions from the Sandia National Laboratory (Albuquerque) and the Development Division at the Y-12 plant.

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\* Note: The SERDP Scientific Advisory Board provided specific guidance to this project. Their position statement on this effort may be found in a separate section within this document; see "Table of Contents."

## **SERDP Thrust Area: Pollution Prevention**

### **Title: Electron Beam Melting and In-Process Scrap Recycling of Uranium**

#### **Problem Statement:**

The goal of the proposed project is to eliminate at least 90% of the depleted uranium waste generated in nuclear weapon component manufacturing. This will be accomplished by using electron beam melting and semi-continuous casting to produce the alloy and by using electron beam melting to recycle in-process scrap generated during thermomechanical component fabrication processes.

Of the uranium which enters the Y-12 (Martin Marietta) complex, the vast majority ends up as waste. Approximately half of this waste is a direct result of producing the alloy and the remaining half results from thermomechanical component fabrication processes. The low yield of the current flow sheet also increases raw material purchased, thereby causing a larger than necessary waste production by the uranium suppliers.

The DOD complex currently uses three consecutive melting steps for the production of uranium alloy ingots. Vacuum induction, skull melting and vacuum are remelting. These melting steps, along with the required cleaning and cutting steps, convert half of the source uranium stream to scrap. In addition, the current melting processes are not suitable for processing uranium alloy chips into high performance materials because of reactions with the graphite crucible during vacuum induction melting and the difficulty of chip consolidation into electrodes for vacuum are remelting. This results in an additional forty percent increase in the required source stream to make up for the waste from forging and machining processes.

The two principal advantages of the electron beam cold hearth refining (EBCHR) process are that the three melting steps can be reduced to one and the process allows the melting and refining of chips. Because the liquid metal pool is contained within a skull of uranium metal which has solidified against the copper crucible, there is none of the refractory contamination pickup common to vacuum induction melting. This allows the melt to be run at high enough temperature to melt alloy in one step, eliminating the induction and skull melt steps. Unlike other heat sources, the electron beam can be moved much faster than the thermal transport speed for heat within the liquid metal. This permits the development and use of optimized beam patterns to accurately control the solidification rate, thermal gradients and fluid flow patterns governing solidification in the mold, eliminating the final arc remelt step.

Metal refining is possible due to the exposure of the molten pool to a hard vacuum. Typical EBCHR product has lower levels of interstitials than in VIM or VIM-VAR material. The flow of metal within the hearth may be controlled to ensure that insoluble material is removed as slag. This allows the refining of scrap materials which may contain undesirable quantities of volatile materials or oxides.

Electron beam melting and refining have been used commercially for the production of ultraclean metals and alloys since the late 1950's. Tonnage quantities of tantalum, niobium, titanium, nickel and iron based alloys are routinely processed using this technique. The use

of EBCHR for the recycling of scrap machine turnings and chips has been an established commercial process in the US since the mid 1970's. Techniques to clean and prepare chips for high vacuum processing, and to feed these noncompactable forms in a semicontinuous mode to an electron beam furnace are well established. Application of this technology to the recycling of scrap uranium alloy promises both economic and ES&H benefits.

The proposed project augments an ongoing development activity in electron beam melting of uranium. SERDP funds would be used to develop the processes for source reduction and cleaning, feeding and casting of the various alloy in-process scrap streams.

#### **Project Description:**

This project will be a joint effort conducted by Lawrence Livermore National Laboratory and Sandia National Laboratory with extensive participation by Y-12. Fundamental process research and optimization will be performed jointly by Lawrence Livermore National Laboratory and Sandia National Laboratory. The uranium melting and casting technology will be developed and demonstrated by Lawrence Livermore National Laboratory with participation by Sandia National Laboratory, Y-12 and other organizations within the weapons complex.

Livermore staff are highly experienced in electron beam melting and casting of uranium. The Uranium AVLIS Program at LLNL has successfully used electron beam technology to melt, vaporize and cast uranium for over 15 years. This technology has reached a level of maturity where ton quantities of uranium are routinely processed. The Sandia staff have extensive experience in electron beam melting and casting research, and a fully operational production scale electron beam melting and casting facility qualified for surrogate material operations. In addition, Sandia staff have made considerable progress on the development of a computer simulation of the casting process in an earlier DOE/DoD funded program.

The AVLIS facility is being modified, using non-SERDP funds, to develop the technology for melting and casting of the required uranium alloys. This facility is fully certified for uranium operations under current ES&H regulations. The plan is to utilize commercial electron beam generation and transport hardware to better facilitate the eventual transfer of this technology to a production facility.

The primary thrust of the project is to perform the research and development necessary to demonstrate and transfer the technology to produce in-spec alloy ingots using both virgin feed and scrap material. The initial SERDP funded technology development work consists of the following elements:

1. Characterize the chemistry of the alloy scrap streams and develop a metallurgical purity specification for the final ingot product.
2. Specify and develop procedures for cleaning of scrap streams and for preparation of scrap for feeding to the electron beam furnace.
3. Carry out basic melting and solidification studies using alloy scrap material from Y-12.

4. Perform research to investigate and computationally model electron beam/molten pool interactions, fluid flow, and heat flow in the hearth and ingot. Benchmark these models with experiments using a surrogate material at Sandia and uranium at LLNL.
5. Perform computer modeling to optimize the electron beam power distribution for the required control of fluid and heat flow in the hearth and ingot.

These activities will go on in parallel with the activation of the uranium alloy melting and casting system at LLNL. Once the furnace becomes operational, alloy and inprocess alloy scrap material will be fed, melted and continuously cast into an ingot product. The material produced will be analyzed for composition, homogeneity and grain structure. This information will be used to benchmark the process models for uranium and further develop the process.

This project directly addresses the DOE and DoD objective to minimize the generation of hazardous and mixed wastes. The program also complements other weapons complex manufacturing pollution prevention and process efficiency improvement programs. Examples include the near net shape casting work being done at LLNL, SNL, and LANL, machine chip cleaning and consolidation work at Y-12, and the arc saw development at Y-12. In addition to DOE and DoD sources, there are commercial uranium processing operations that do not currently recycle scrap. This technology has the potential for eventual transfer to the commercial sector.

The project is funded with non-SERDP, as well as SERDP money. SERDP funds are allocated primarily to development and demonstration of the basic melting and casting process. Non-SERDP funds are used to modify and activate the LLNL uranium melting and casting system, and to perform tasks related to design and deployment of a production prototype unit. Key tasks for the jointly sponsored project are listed below; more detail on specific allocation of monies appears in the section of the proposal on funding:

1. Design, build and activate the uranium melting and casting furnace (LLNL)
2. Perform research, develop and benchmark computer codes to describe relevant physics in hearth and ingot. (LNL/SNL)
3. Demonstrate techniques for casting an alloy ingot from virgin uranium feedstock (LLNL).
4. Develop techniques for cleaning, feeding and melting of machine chips and other scrap materials (LLNL/Y-12).
5. Demonstrate production of an in-spec. ingot from alloy scrap material (LLNL).
6. Optimize process for product purity, homogeneity, and grain structure. (LLNL/SNL).
7. Design a production prototype melting and casting unit based on experience gained from the development system (LLNL/Y-12/SNL).
8. Build and operate production prototype system (LLNL).

The key technical challenges are to develop the required level of process understanding and control to allow the metallurgical goals to be achieved, and to develop the feed preparation and delivery techniques needed for scrap recycle.

#### **Expected Payoff:**

The goal of the proposed project is to eliminate at least 90% of the waste generated in component manufacturing. Minimization of depleted uranium waste, and development and demonstration of a process which can be implemented at manufacturing plants, will support the DOE's and DoD's environmental goal for pollution prevention and process efficiency. Electron beam processing will permit a single step production of high quality alloy ingots, and the recycling of in-process scrap, both of which reduce the source stream and allow a substantial reduction of waste streams. Once accomplished, the reuse of stored scrap and the demilitarization/disposal of obsolete ammunition will be added benefits.

Aside from source reduction and in-process recycling, this project provides reduced costs, improved operations and reduced ES&H liabilities.

#### **Milestones:**

During the execution year, the following activities will be completed:

1. Complete design, fabrication and activation of a development electron beam melter and ingot caster (Non-SERDP funds).
2. Produce an ingot from virgin uranium feed which meets metallurgical homogeneity and purity specifications.
3. Produce an ingot from Y-12 scrap material.
4. Complete initial experiments and develop computer models to characterize beam/pool interactions, thermal distributions and flow fields in the hearth. Write a report documenting results of analysis.
5. Complete a report documenting the results of the activity and outlining a plan for process optimization, and design of a production prototype unit.

#### **Transition Plan:**

The proposed activities will be performed to support LLNL's role as lead lab for uranium manufacturing. All work will be performed in close conjunction with Y-12 and other organizations in the weapons complex. This technology could also be used by Picatinny (Army), Wright Laboratory Armament Directorate (Air Force) and complements the weapons complex modernization. Initial transfer of the technology will be accomplished by staff interaction among the potential user organizations. The objectives of this program are the research, understanding and demonstration of the technology. Follow up activities include optimization studies and development of a process design package and facility

implementation plan for installing a production electron beam furnace unit at a DoD and/or DOE manufacturing/recycling site.

**Funding: (\$K)**

Design and fabrication of the melting and casting furnace at LLNL is funded at \$1.85M for FY93 with non-SERDP funds. Y-12 is supporting the facility activation with \$100K for non-SERDP funds. Requested SERDP funds are \$1.3M for FY93 and will be used as follows:

	FY93
Production of an in-spec. ingot	545K (LLNL)
Production of an ingot from Y-12 scrap	275K (LLNL)
Supporting research activities, including development and benchmarking of computational models	300K (SNL) 180K (LLNL)
Total	1,300

In addition, LLNL will provide matching non-SERDP funds of approximately \$1.45M in support for the SERDP project as follows:

Mechanical, electrical and management support	125K
Design, fabrication and activation of the scrap	77K
Documentation	100K
Process optimization and prototype design studies	400K

Any SERDP funding beyond the initial performance year will be used to extend the capabilities of the electron beam process and to support process optimization in the following areas: carbide removal, minimization of vaporization, reduction in personnel exposure, solidification structure control and ingot optimization. Of particular interest are development of process technologies to remove carbides from the scrap and to minimize vaporization during the melting the casting process. Carbide removal would allow the recycle of particularly difficult material, such as hot tops, which currently must be stored or disposed of. Process optimization to minimize uranium vaporization during melting and casting would further minimize the waste streams.

Non-SERDP funding beyond the initial performance year will be used to enhance the baseline process and to design, build and operate a production prototype melting and casting system.

**Performers:**

Participants in this project will include staff from LLNL, SNL and Y-12. Other participants may include personnel from DOE production agencies such as the Army, Air Force and those associated with the weapons complex modernization.

Our plan is to rely heavily on industrial participants to provide electron beam generation and transport systems and continuous casting systems. We will also propose cooperative research agreements with existing commercial uranium operations which would benefit from the recycle of scrap materials.

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Continuous Oxide Reduction System (CORS)**

#### **Problem Statement:**

A continuous oxide reduction reactor will be developed for converting actinide oxides (i.e., uranium or plutonium) to metal. The reactor incorporates direct oxide reduction (DOR) technology, reducing the oxide to metal with calcium and subsequently solvating the resultant calcium oxide in molten calcium chloride. To maintain continuous operation and reduce waste, the calcium oxide is continuously converted into calcium chloride. The initial small scale reactor has projected throughput of 1 kg per two hours. The salt waste is expected to be 1 kg per 1 kg of actinide metal produced, an 80% reduction compared to conventional processing. Additional applications of this technology include the treatment of waste calcine at the Idaho Chemical Processing Plant (ICPP) and Rocky Flats Plant (RFP) reactive salt disposal.

The reduction of actinide compounds to metal is required for various processes. Uranium metal feed is needed for Uranium-Atomic Vapor Laser Isotope Separation (U-AVLIS) processes and for fuel in the IFR type nuclear reactor. Plutonium metal is required for DOE defense programs. The current processes to produce metallic actinides are generally multiple batch processes that have low throughput; are labor intensive; result in personnel radiation exposure; and generate significant amounts of waste.

Uranium metal is currently produced from the oxide by first reacting uranium oxide with hydrogen fluoride to form uranium hexafluoride. The uranium hexafluoride is then reduced using calcium or magnesium metal to produce the uranium metal and a calcium or magnesium fluoride salt. The short comings of this process are:

- Multiple processing steps are required;
- Final reduction operation is a labor intensive batch process;
- Large volumes of contaminated solid waste are generated;
- Substantial quantities of uranium are lost without waste reprocessing, and
- Hydrogen fluoride gas is one of the more toxic halogenated gases.

Other proposed processes for uranium metal production are uranium oxide/fluoride electrolysis, uranium chloride electrolysis, and continuous metallothermic reduction of uranium chloride. All of these processes require unit operation for converting uranium oxide to a chloride or fluoride before reducing it to metal. The electrolysis processes are inherently slow and thus require many units to achieve reasonable capacity. The Saltless DOR (SDOR) process is being developed by Martin Marietta (Y-12 plant) for converting uranium oxide to uranium metal. This process also requires several unit operation.

The Idaho Chemical Process Plant (ICPP), located at the Idaho National Engineering Laboratory (INEL), has reprocessed irradiated nuclear fuels to recover various radionuclides since 1953. The high-level liquid waste (HLLW) from this reprocessing has been and is being calcined to form a dry granular powder. The calcine is stored in stainless steel bins that are in concrete vaults. The calcine is a mixed hazardous waste that required disposal. This



waste contains less than 1 wt % of long-lived radionuclides that require extended storage, such as in the geological repository. Separating the radionuclides from the inert components would significantly reduce the disposal cost of the ICPP calcine.

The RFP currently has 946 cubic yards of mixed waste that requires disposal. About 246 cubic yards (26%) of this waste is classified as mixed waste because it contains reactive free metals such as sodium, potassium, calcium, or magnesium. These wastes are a result of previous pyrochemical operations at RFP. These reactive metals need to be passivated prior to disposal. A batch passivation process is expected to be setup at RFP in FY 95. The expected throughput of the facility is nominally 2500 kg per year. Using this throughput, the waste is expected to be treated no later than FY 2004. This is beyond the requested completion date of January 1, 1999.

The technical feasibility study for this process was funded with internal research and development money (LDRD) at Lawrence Livermore National Laboratory (LLNL) in fiscal year FY92.

### **Project Description:**

In FY 92, material compatibility testing, equipment fabrication, and process testing were performed. The material compatibility tests demonstrated that magnesium oxide is superior to quartz in the process environment. An integrated reactor was designed and fabricated. Reactor components were successfully tested with individual operational steps. These tests included the DOR operation, salt regeneration, and product removal. The processes were also tested together.

The objective of this program is to develop and demonstrate a integrated reactor for continuous oxide reduction with salt regeneration.

The approach that will be taken to achieve the objective will be to evaluate material compatibility for long term operation, establish operational parameters, collect engineering data for prototype system design, design, fabricate, and install prototype system, and to demonstrate prototype system.

The CORS process matches well with the objectives of the DoD and Doe environmental objectives. The use of the CORS would reduce waste due to its internal salt regeneration as well as the inherent waste volume advantage that pyrochemical processing has over aqueous processing. It would also decrease processing time because the process will run continuously. The continuous operation also requires less operator intervention. This reduces the operator radiation exposure.

There are other oxide reduction efforts mentioned in the background section. This is the only work we are aware of for continuous reduction.

In FY 93, the long term testing of the process with surrogates will be under way. The testing will also help to identify the important engineering variables. In Fy 94, the small scale reactor will be demonstrated with uranium. A uranium-iron alloy will be used to decrease the melt temperature. The principal parameters to be examined are process yield, throughput,

equipment corrosion and chlorination efficiency. This testing will provide the engineering data necessary for the design of a prototype uranium system.

In FY 95, a prototype uranium system will be designed, fabricated and installed. The uranium system will be tested with depleted uranium. The initial system testing will be with surrogates. Final prototype reactor demonstration with uranium or other actinides will be performed in FY96.

The technical issues to be addressed are long term material corrosion issues, and material compatibility verification for use with uranium at the higher temperatures.

#### **Expected Payoff:**

The potential users of this process include government and private industry. This technology would benefit DoD/DoE defense program plutonium and uranium operations by significantly increasing throughput, thus minimizing space in high hazard facilities. The process will also require little operator intervention, decrease radiation exposure, and significantly reduce that amount of process waste. This technology can be used in existing plutonium and uranium operations or can be incorporated into new facilities.

A proposed method of purifying uranium is by using the U-AVLIS process. This process requires uranium in metal form. The CORS generates metal from the oxide in fewer steps, with less radiation exposure, and higher throughput than other processes. General Electric has also expressed an interest in using this technology in the reprocessing of light water reactor fuel using a molten salt-metal cycle.

This technology can also be used for waste processing. The RFP reactive salts and ICPP calcine wastes can be treated using the CORS. The RFP reactive salts contain reactive metals. The processing of this waste is estimated to require 9 years using a batch process. Using the CORS could reduce the processing time to 2 years. Using the CORS with ICPP could reduce the high-level waste requiring disposal by a factor of 30 without a significant increase of total waste. This would significantly decrease the cost and volume required for disposal of this waste.

#### **Milestones:**

Long Term Testing	FY93-94
Uranium Demonstration	FY94-95
Design, fabricate, and install a prototype uranium system	FY94-95
Surrogate testing of Uranium Reactor	FY95
Testing Uranium reactor with depleted Uranium	FY96

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
371	900

**Transition Plan:**

There is ongoing discussions with representatives from U-AVLIS, RFP, INEL and General Electric for the use of CORS. Investigation of this technology for Complex 21 is part of the uranium processing lead lab development plan.

**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

**Title:** Application of Supercritical Fluid Extraction and Supercritical Fluid Chromatography to Analysis of Energetic materials

### **Problem Statement:**

Large quantities of explosives--contaminated hazardous solvent wastes are being generated in the chemical laboratories within DoD, its GOCO plants, and associated contractor laboratories which perform the analyses of energetic and related materials. The objective of this project is to essentially completely eliminate (>99%) the generation of such wastes through the implementation of the proposed analytical methodologies combined with solvent recovery.

The targeted department/organizations are all DoD ammunition plants, contractors, and R&D Centers performing the analyses of energetic and related materials.

### **Project Description:**

This project will evaluate supercritical fluid extraction (SFE), supercritical fluid chromatography (SFC), high resolution, high performance liquid chromatography (HRHPLC), and solvent recovery of energetic materials to eliminate greater than 99% of hazardous waste solvents and reagents with added advantages of attaining shorter analysis time and more reliable results. This is a 6.3A level of effort.

### **Expected Payoff:**

The economic benefits of this project include solvent and chemical reagent cost savings estimated to be greater than \$200,000 per year, the waste disposal cost saving, and the labor cost savings from shortened analysis time. In addition, this project will bring health, safety and better quality control benefits including minimization of exposure of laboratory benefits including minimization of exposure of laboratory personnel to toxic solvents and reagents, minimization of solvent and reagent fire hazards, and more reliable analytical results.

### **Milestones:**

Procurement and setting up of SFE/SFC/HRHPLC and solvent recovery systems	FY93-94
Development of analytical methodologies for the analyses of energetic and related materials and solvent recovery	FY93-95

### **Transition Plan:**

New procedures disseminated for the analyses of energetic and related materials and solvent recovery system, and publication of new analytical specifications and solvent recovery.

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
200	220

**Performers:**

The performer is the U.S. Army Armament Research, Development and Engineering Center, Picatinny Arsenal, NJ

**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

**Title:** Depleted Uranium Waste Minimization and Material Reutilization

### **Problem Statement:**

Burial of low specific activity waste is becoming ever increasingly expensive. Availability of burial sites is also a concern. The intent of this effort is to minimize the volume of waste which the DoD disposes of through burial. The objective of this study is to develop technology that will permit the recycle of machining chips and grinding back into the processing stream for the manufacture of Kinetic energy penetrators.

### **Project Description:**

This effort will focus on developing electron beam, cold hearth vacuum furnace technology to convert DU machining wastes into billets for production uses. Chemical reprocessing recovery investigations being conducted within the Department of Energy (DOE) complex will also be considered for applicability to DoD needs.

A production size, fully instrumented electron beam vacuum furnace exists at the Sandia National Laboratories. This unit will be utilized to develop operational process parameters for depleted uranium. Present chemical reprocessing of enriched uranium within the DOE is technically and environmentally unsuitable for translation to reprocessing of DU oxides. However, present proposed studies to improve this processing may make it suitable for DU reprocessing.

### **Expected Payoff:**

This project will drastically reduce burial of low specific activity waste associated with the manufacture of depleted uranium (DU) penetrators and other items.

### **Milestones:**

1. Develop computational model to simulate interaction between electron beams and fluid flow within hearth and billet (0-12 months)
2. Bring furnace to operational status (0-12 months)
3. Develop operational process parameters for titanium alloys (12-24 months)
4. Develop operational process parameters for uranium alloys (12-24 months)
5. Technology transfer to commercial sector (furnace design) (24-36 months)
6. Demonstration of technology in production (36-48 months)

### **Transition Plan:**

This project is included in the DoD Strategic R&D Plan and is depicted on roadmap # 3.C/DU Waste Elimination.

The Coordinator between user and performer was accomplished during a pollution prevention user review in July 92, a peer review in Aug 92 and the recent DoD Strategic Environmental R&D review during 7-11 Dec 92.

Briefings to Government and Industry audiences were given at the ADPA environmental symposium at Picatinny Arsenal, 20-21 Oct 92 and the AMCCOM Advanced Planning Briefing to Industry 28-29 Oct 92 at Rock Island, IL.

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
350	425

**Performers:**

Sandia National Laboratories, Penetrator Manufacturer.

**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

**Title:** High Efficiency Magnetic Bearing Lubrication Free Centrifugal Compressor For Use with Environmentally Safe Alternate Refrigerants

### **Problem Statement:**

The goal of this project is to conduct a field demonstration of a high efficiency lubrication free compressor that allows the use of various environmentally safe alternate refrigerants. The proposed alternate refrigerants are intrinsically less stable than the currently used CFCs. The introduction of a lubricant into these working fluids further lowers the thermal stability to the point that the fluid could decompose in the system, thus limiting many high temperature installation configurations and significantly reducing system life in both aircraft and ground equipment applications. The U.S. Air Force is the targeted organization of this project.

The use of CFCs and even HCFCs will be outlawed by 1995 by the EPA's Clean Air Act. Alternate heat pump and refrigeration systems utilizing these new refrigerants have been proposed as possible replacements but use much lower efficiency cycles such as Stirling, Brayton, Magnetic, Sonic or Chemical. These cycles will result in much less efficient and heavier systems. But the development of a lubrication-free magnetic bearing compressor, when coupled with an alternate working fluid enables the continued use of centrifugal compressor technology. The use of this technology also allows for the possible retrofit of current systems, at considerable cost savings. Only the compressor and working fluid are changed.

This is a new program is based on technology developed on several SDIO Phase 2 SBIR programs and prior SDI sponsored applied research efforts relating to high temperature "lift" heat pump concepts.

### **Project Description:**

The technical objective of this program is to develop a high efficiency lubrication-free, magnetic bearing compressor that allows the use of environmentally safe alternate refrigerants with improved system efficiencies over current SOTA technology.

A feasible approach to this project is to couple the recently developed 3-D compressor modeling and automated fabrication technologies with magnetic bearing technology and then demonstrate the performance, life, reliability and overall thermal performance of the compressor.

The technical tasks for this project are to iteratively design and test 3-D impeller/diffuser sets, using this experimental data base to improve the theoretical technology base. Three iterations will be accomplished, the final being the optimized compressor system. Development of a CFC free compressor would allow the continued use of vapor compression refrigeration systems without any environmental problems.



The basic feasibility of these technologies was developed on SDIO funded SBIR programs managed by Wright Laboratory. The technology was initiated for use as a long-life, high reliability heat pump for spacecraft thermal control. Although the feasibility of the individual components has been shown, the unit still needs to be demonstrated as an integrated system.

#### **Expected Payoff:**

This compressor has vast military, commercial, residential and industrial applications and tremendous payoff. It has the capability of replacing the CFC and thus solving the environmental problem with a net performance enhancement because of the highly efficient 3-D compressor design. The 3-D compressor has the promise of compressor efficiencies approaching the upper 90% range, which compares very favorably with current SOTA 2-D compressors efficiencies, typically 70%. It is cost effective since a retrofit program would involve only the compressor and working fluid, not the entire system. It is capable of variable speed and has integral diagnostics.

The military applications include aircraft environmental control systems, ground support equipment, spacecraft thermal control, oil-free hydrogen compressor for proposed battlefield fuel cell applications and as an aircraft oil-free compressed air generator.

The other applications include the vast residential and automotive air conditioning and heat pump market, and commercial chiller requirements. Application of this technology is not only environment enhancing, but also provides immense energy efficiency and energy cost benefits.

#### **Milestones:**

This is a projected two year program. At the completion of the first year, the compressor will be designed, the test rig designed and built, and the compressor parts manufactured.

#### **Transition Plan:**

After this program demonstrates the integrated system, the technology will move to the engineering development stage and optimized for specific applications. Coordination will be maintained between the contractor and potential users. The contractor will have the ability to assume production at the completion of the program.

#### **Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
250	250

#### **Performers:**

The agency laboratory is Wright Laboratory at WPAFB, Ohio. The industry involvement will be with Mainstream Engineering Corporation in Rockledge, Florida and SatCon Technology

in Boston, Massachusetts. A planned cooperative development agreement is possible between WL, Mainstream and SatCon.

**Technical Point of Contact:**

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**SERDP Thrust Area: Pollution Prevention**

**Title:** Research in Chlorofluorocarbon (CFC) Substitutes

**Problem Statement:**

The goal of this project is to research potential alternative refrigerants to replace chlorofluorocarbons (CFCs) for use in microclimate refrigeration equipment. Specifically, the objective is to evaluate alternative refrigerants' thermodynamic properties and examine their effects on performance, operating pressures, lubrication, etc., in current developmental microclimate refrigeration equipment.

**Project Description:**

The project will test compatibility of alternative refrigerants with lubricants under different operating conditions. Microclimate cooling (MCC) systems will then be modified to run efficient when using the new substances. This will include determining the optimum operating temperatures, pressures, etc., for different environmental conditions. Components will also have to be examined and may require redesign in order to meet the goals. This is a 6.3A level of effort.

**Expected Payoff:**

By replacing CFCs at this stage of MCC systems development, time and money will not be wasted in the development of MCC systems designed to operate on CFCs. CFCs are to be phased out by 1995. Any use of CFCs after this date will carry a heavy fine (tax). By replacing them now, the system designed to operate on alternative refrigerants can be released earlier and there will be no need to retrofit systems designed to run on CFCs. The system will be more energy efficient and environmentally safe than CFC systems.

**Milestones:**

This project must examine the problems associated with alternative refrigerants and compatible lubricants. There are problems with chemical stability, reactivity, lubrication, water absorption, etc. By the end of FY93 these problems will be resolved.

**Funding: (\$K)**

	FY93
SERDP	100
Service Funds	50

**Performers:**

Natick Research, Development and Engineering Center, LSSD/IPD/Special Projects Section.  
Coordination with University of Illinois

**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Encapsulated Micron Aerosol Agent (EMAA) Technology**

#### **Problem Statement:**

The goal of this project is to develop a fire suppression agent that does not create undesirable environmental impacts.

The Air Force is facing an ever increasing problem with several fire suppression agents that, while very effective at their main function of extinguishing fires, also create undesirable environmental impacts. For example, aqueous film forming foam (AFFF) is an excellent extinguishant for two-dimensional pool fires that occur on Air Force flight lines or as a result of aircraft accidents and crashes. However AFFF, due to its surfactant content, can become an unpleasant, soapy constituent of ground water if it flows into an uncontrolled area. The Halon family of fire suppression agents, while very powerful fire extinguishants, must be replaced due to their ozone depletion potential (ODP).

The problem then is to find a class of environmentally benign fire suppressants that are as powerful as AFFF and the Halons. Extensive research to this point in time has indicated that currently available chemicals are not as effective fire suppressants as AFFF and Halon 1301, resulting in limitations in applications and training, as well as space/weight/cost penalties. Totally new approaches to fire suppression were not originally factored into the AFFF and Halon 1301 replacement program because no new concepts had surfaced until the recent emergence of aerosol fire suppressants. Biodegradable replacements for AFFF have not yet been found. Halon 1301 replacement candidates identified thus far are 2-3 times less effective than Halon 1301 in fire suppression efficiency.

The candidate down-selected as the replacement agent will require major modifications to piping, nozzles, and other components of the delivery systems. Additionally the basic delivery concept of total-flooding of the affected areas remains unchanged, resulting in unnecessary emissions of fire suppressants to the atmosphere. The bottom-line is that a class of environmentally safe fire suppressants is badly needed and required to maintain the operational readiness and capability of the Air Force. This is a new program.

#### **Project Description:**

The technical objective of this project is to investigate the capabilities of a totally new class of fire suppressants known as aerosols that have emerged in the international literature. At a 1990 Conference in Geneva, Soviet scientists described the development of aerosols that, fabricated from cheap, readily available materials, had very powerful fire suppression characteristics.

The aim of this project is to evaluate and test these aerosols on a laboratory scale that simulates operational conditions to suppress fires in enclosed space. On a weight basis the aerosols are 5-6 times more powerful than Halon 1301. The generic name given to these materials is "Encapsulated Micron Aerosol Agents" or EMMA. EMMA is initially in a solid, powder, or gel form that is pyrotechnically started, generating an aerosol that behaves as a

lighter than air gas. The initiation may be by active signal from a fire detection system or may be by passive self-initiation. EMAA may provide the Air Force with an environmentally and occupationally safe agent that has zero ODP, zero GWP, very low toxicity, and low life cycle costs. EMAA systems require no piping or pressure cylinders and will be a fraction of the cost of Halon 1301 in installation and life cycle costs. It also allows delivery strategies other than total flood and can be placed locally in high fire risk locations within a facility.

In addition to facility applications, EMAA has been demonstrated to be effective against fuel tank fires. It can be located at the bottom of a fuel storage tank and then set off when a fire is detected. The resulting aerosol percolates to the surface and quickly extinguishes the fire. A wide range of other applications for EMAA technology is envisioned to include UPS rooms, battery rooms, generator rooms; communications, electronics, computer facilities; aircraft dry bays, engine nacelle protection, and modular buildings for rapid deployment forces. Various EMAA formulations will be tested for fire suppression efficiency, materials compatibility, storage stability and lifetime, packaging, toxicity, electrical conductivity, corrosion, and combustion products. The results of these analyses will be utilized in the engineering of delivery systems for both total-flood and local fire suppression strategies. Several EMAA formulations will be tested in laboratory cup burner and fire box configurations to determine the fire suppression mechanisms and fire suppression efficiency of the aerosols. A key issue to assess is the corrosion effects of the aerosols to determine if the aerosols are detrimental to electronic components or other materials. Several delivery packages and methods containing both non-electrical and electrical initiation will be designed, fabricated, and tested to determine the best practical methods for delivering fire suppression aerosols. Ultimately, large scale testing against scenario fires will be conducted to determine the final configuration of EMAA delivery systems. Toxicity assessment will be conducted by Armstrong Labs for neat agent, thermal decomposition products, and combustion products.

This project is not in the AF Environmental Quality Research, Development and Acquisition Strategic Plan and the Tri-Service Environmental Strategic Plan under the DoD Pillar 3 by name, but it does act as a compliment or substitute for any additional agent developed to replace Halon 1301.

#### **Expected Payoff:**

The successful development of EMAA technology and its delivery systems will provide the Air Force with a broad range of fire suppression agents that are not only state-of-the-art in fire extinguishing capability, but are also environmentally safe. EMAA systems will be able to protect all types of facilities, storage areas, fuel storage tanks, and possibly have aircraft fire suppression roles.

#### **Milestones:**

Selection of aerosol formulations	Jun 93
Fire suppression effectiveness	Dec 93
Toxicity, stability, and corrosion	Jun 94
Small scale tests	Sep 94

**Transition Plan:**

Establishing a CRDA between the Air Force laboratories and Spectrex, Inc. to produce a powerful yet low cost fire protection system. Provisions in the CRDA create devices that are suitable for Air Force and DoD applications. The Air Force Center for Environmental Excellence's Technology Transition Division will be continually advised of the status of this research and will assist in the transition throughout the Air Force, to other federal agencies, and to the private sector.

**Funding: (\$K)**

FY93	FY94	Total
650	350	1000

**Performers:**

The USAF Wright Laboratory, Flight Dynamics Directorate in conjunction with CRDA and in-house contractor.

U.S. Air Force/HQ AFCESA/RACF:	Dr. Charles J. Kibert	(904) 283-3734
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SETA Contractor:	Mr. Michael Rochefort	(904) 286-5070
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U.S. Air Force/AL OET: Toxicity Testing	Lt Col James McDougal	(513) 255-1474
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Spectrex, Inc.:	Mr. Eric Zinn	(201) 239-8398
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NMERI:	Dr. Robert Tapscott	(505) 272-7252
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**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

**Title:** Chemical and Physical Processes Responsible for Flame Inhibition Using Halon Agents and Their Alternatives

### **Problem Statement:**

This research program is aimed at elucidating the detailed chemical and physical processes that are responsible for flame extinguishment. This will be accomplished by a coordinated experimental and modeling effort on flame suppression chemistry. Toxic and non-toxic Halon-substitute combustion products will also be identified and measured by laser spectroscopic and mass spectrometric means.

Currently there is a great need to identify new Halon alternatives for Army-specific fire fighting applications. The expectation that industry will supply an adequate number of Halon alternative compounds has not been met. Therefore, the Army is facing a potentially very serious gap in providing fire fighting capability for current and future combat vehicles.

### **Project Description:**

This research will be accomplished by means of detailed experimental kinetic and flame structure studies coupled with computer simulation models. The aim of this research is the understanding of the chemical and physical mechanisms underlying flame suppression. This knowledge, in turn, will lead to the identification of new classes of fire suppressants.

This research will be conducted using a highly instrumented laboratory burner apparatus which includes molecular beam mass spectrometry and laser spectroscopic techniques for species and temperature profile determinations in a laminar flow premixed flame. This flame research apparatus will also be used to determine relative flame quenching characteristics of specific Halon alternative candidates which have been recently identified by the Air Force and those that will be identified in the future. In addition to the premixed flame chemistry research, kinetics experiments will be performed to generate thermal rate constant data relevant to flame intermediate species, such as  $\text{CF}_3$  and  $\text{CF}_2$ , which are common to all gaseous flame extinguishers. This kinetic data is necessary input into the detailed chemistry flame models. For the special cases where important rate constants are difficult to determine directly by experimental means, we will calculate them using quantum chemical techniques resident within the ARL quantum chemistry group. Toxic and non-toxic Halon-substitute combustion products will also be identified and measured using laser spectroscopic and mass spectrometric means.

Flame extinction can be accomplished by powders as well as by gases. The flame extinguishment mechanism for powders is anticipated to be quite different than that for the gases, involving thermal processes as well as possible heterogeneous chemistry. Since the eventual replacement(s) of presently used Halons may be a powder, our study will also include kinetic measurements of the relevant heterogeneous reactions.



The use of state-of-the-art flame diagnostic and kinetic measurements coupled with advanced computer simulation models represents a novel approach to the important problem of identifying new environmentally-acceptable fire extinguishing compounds.

#### **Expected Payoff:**

The U.S. Army Material Command is charged with providing combat vehicles with the ability to extinguish crew compartment fires. The current method of meeting this requirement is the use of total flooding Halon 1301 systems. Clean Air legislation and Army Regulation 70-68 dictate the cessation of the purchase of any new Halons by October 1995. Since these regulations were enacted, data from atmospheric monitors indicate a much larger loss of stratospheric ozone than expected. This, in turn, has led to an accelerated phase-out of Halon production and use.

#### **Milestones:**

The recently approved "Technology Strategy on Alternatives to Ozone-Depleting Chemicals (ODCs) for Weapon Systems Use" stipulates the identification of Halon alternative fire extinguishers by FY96. In view of this urgency, we will aspire to accelerate the research as much as possible as well as to disseminate our interim useful findings to the appropriate agencies and activities.

Initiate kinetic studies of important flame extinction intermediates, such as CF<sub>3</sub> and CF<sub>2</sub>. FY93

Develop kinetic and thermochemical data base to be used by flame models.

Compare flame structure of hydrocarbon flames with current and proposed flame suppressors.

Calculate selected rate constants by quantum chemical methods.

Develop detailed chemistry flame mechanisms relevant to flame extinction. FY94

Complete gas phase kinetic studies.

Test and validate the detailed chemistry flame models. FY95

Kinetic studies of heterogeneous reactions relevant to powder flame suppressants.

#### **Transition Plan:**

There has been considerable fundamental work done on flame inhibition throughout the 1970s and into the early 1980s. This basic research ceased abruptly when the viable flame extinguishers Halon 1211 and Halon 1301 were fully characterized, tested, and deemed acceptable for practical use. The state of fundamental knowledge at the point where further work ceased can be characterized as educated speculation, particularly as to the roles of HBr and CH<sub>3</sub>Br in the catalytic recombination of hydrogen atoms. Unfortunately, virtually all of the previous work had been conducted on bromine-containing compounds, whereas the likely Halon alternative compounds of the future will not contain bromine, but rather mostly fluorine. Thus, a new effort on fluorine flame chemistry needs to be initiated in order to make further progress on the understanding of flame inhibition.

**Funding: (\$K)**

	<b>FY92</b>	<b>FY93</b>	<b>FY94</b>
SERDP Ph. I			
In-House	125	250	325
Contract	0	50	75
Total	125	300	400

**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

**Title:** VOC (Volatile Organic Compound) and Hazardous Air Pollutant (HAP) Emissions Reduction for Painting, Cleaning, and Vapor Degreasing Facilities at Marine Corps Multi-Commodity Maintenance Centers

### **Problem Statement:**

It is the goal of the Marine Corp Multi-commodity Maintenance Center (MC)<sup>3</sup>s to work cooperatively with the Environmental Protection Agency to demonstrate, evaluate, and improve innovative pollution prevention and control technology approaches which can be used to reduce air emissions from painting, cleaning, and vapor degreasing facilities at the (MC)<sup>3</sup>s and other similar military installations. The research planned will support the combined goals of the (MC)<sup>3</sup>s and the USEPA Air and Energy Engineering Research Laboratory (AEERL), co-sponsor of this proposal, to achieve rapid improvement in the quality of air emissions from paint spray booths and vapor degreasing tanks at (MC)<sup>3</sup> Barstow and (MC)<sup>3</sup> Albany and develop information on advanced air pollution prevention and control approaches applicable to problems in the private sector. Research results from the field tests at (MC)<sup>3</sup> Barstow and Laboratory research underway at the Applied Research Laboratory, the Pennsylvania State University (ARL Penn State), and AEERL will be used to upgrade the installed system at Barstow, will be applied to a second set of systems at (MC)<sup>3</sup> Albany, and will be immediately available for transfer to both other DoD operations and private industry. Effective technology transfer will be facilitated by the USMC and AEERL through reports and other appropriate delivery mechanisms.

The Marine Corps is aware of several technologies available to decrease the emissions from paint spray booths and vapor degreasing tanks. Among these technologies, UV-oxidation systems show promise as cost-effective emission reduction approaches for the processes used at the (MC)<sup>3</sup>s. In addition, the AEERL has developed methods for reducing the air flow rates from spray booths which must be treated by a technology. ARL Penn State has demonstrated the potential of laser, ultra violet radiation, and other coherent energy sources in the destruction of VOC's. In addition, EPA is in the process of defining alternative processes and compounds which eliminate VOC emissions from surface cleaning operations including degreasing. The (MC)<sup>3</sup>s believe that a joint effort by these organizations can result in an immediate benefit to (MC)<sup>3</sup> Barstow and Albany and a substantial improvement in the capabilities of cost effective Air Pollution Control Systems (APCS) for emission problems similar to those at the (MC)<sup>3</sup>s. This is a request to initiate a new project.

### **Project Description:**

The team which will execute the program for (MC)<sup>3</sup> has amassed a substantial technical and program management background which prepares it well. TAES has designed, fabricated, and installed three systems for General Dynamics, one for Northrop (B-2 Division), and numerous others for non-defense related industries. One of General Dynamics systems, installed at Pomona Naval Weapons Laboratory, received the "First Annual Award for Innovative Technology" from the South Coast Air Quality Management District of California.

ARL Penn State will apply the technical expertise of a team which will include Dr. Robert J. Heinsohn, Dr. William H. Brune III, and Dr. Dennis Lamb. Their research areas include topics essential to program success, such as:

Photochemistry of atoms and molecules  
Chemical and physical processes relating to airborne pollution  
Atmospheric air pollution modeling  
Photodissociation and radical oxidation process for the destruction of VOC's

The USEPA Air and Energy Engineering Research Laboratory has over a decade of experience evaluating and developing emission reduction approaches for Volatile Organic Compounds and Hazardous Air Pollutants. AEERL has extensive expertise developing and designing advanced recirculation approaches for spray booths and identifying alternative approaches for surface cleaning applications. The majority of AEERL's previous spray booth research has been conducted jointly with the Air Force (Dr. Joseph Wander, (904) 283-6026).

The program is intended to:

- Result in substantial VOC and air toxic emissions reductions at (MC)<sup>3</sup> Barstow and Albany and wherever similar systems are installed
- Demonstrate and continuously improve technology for the destruction of VOC's through coherent energy sources and radical oxidation processes
- Enhance the understanding of the use of coherent energy sources which initiate radical oxidation processes to destroy VOC's
- Enhance the understanding of air recirculation in paint booths to decrease the overall volumetric air flow rates
- Apply lessons learned in modeling and experimentation to the design of optimal VOC control system configurations
- Enhance the understanding of the emission reduction potential of TAES and other advanced VOC destruction technologies tested under this multi-year program.
- Determine the feasibility of solvent substitutes for surface cleaning operations including degreasing which meet the specific needs of (MC)<sup>3</sup> Barstow and Albany.

The program is designed to have full scale equipment operating (funded through non-SERDP USMC funds) at (MC)<sup>3</sup> Barstow, while laboratory research is conducted simultaneously at ARL Penn State and EPA. This approach will allow rapid evaluation of field data in the lab, and application of optimization techniques in the field immediately after they have proven themselves in the laboratory setting. A recirculating paint booth of EPA design and at approximately 30,000 CFM TAES APCS will be installed and run at (MC)<sup>3</sup> Barstow. The TAES APCS will be connected to paint and cleaning booths so as to treat either stream of emission. Data will be collected while this equipment is used to accomplish the (MC)<sup>3</sup> production schedule. Modeling and experimentation at ARL Penn State and EPA will feed an iterative cycle of enhanced understanding of the processes, optimization of the field systems and additional data collection. EPA will generate base line data by conducting a through air emissions inventory at the depot prior to running the new equipment. EPA will also initiate efforts to define potential product substitution options for the solvents currently used by the (MC)<sup>3</sup> for their degreasing operations. The most promising options will be evaluated at Barstow and Albany. A second set of systems, upgraded to take advantage of

the knowledge acquired in the program, will be installed at (MC)<sup>3</sup> Albany during the second year of the program.

The program will enhance the (MC)<sup>3</sup>'s ability, and subsequently the ability of other DoD and industry facilities, to accomplish their missions while complying with local, state, and federal environmental regulations. The program will add to the body of knowledge relating to VOC emissions, and will, through technology transfer efforts, bring improved systems to the market place very quickly.

The New Jersey Institute of Technologies (NJIT) and The Pennsylvania State University's Environmental Research Resource Institute (ERRI) are sponsoring research at Penn State to investigate photodissociation and radical oxidation processes as they relate to the destruction of VOC's. This research now underway will contribute directly to the (MC)<sup>3</sup> program.

AEERL is working cooperatively with the Air Force on related spray booth research (\$500K in FY-92 was provided to AEERL). In addition, AEERL plans to spend \$500K in FY-93 on related surface cleaning projects which will directly benefit the research proposed for Barstow and Albany.

#### Tasks/Activities

The program (includes SERDP and non-SERDP funds) will include the following tasks:

1. Complete inventory/assessment of (MC)<sup>3</sup> VOC emissions by EPA
2. Specify and install TAES system at (MC)<sup>3</sup> Barstow (USMC funds)
3. Design recirculation modifications for paint spray booths at (MC)<sup>3</sup> Barstow
4. Install and calibrate instrumentation for TAES APCS and recirculating paint spray booths
5. Acquisition of equipment and set up lab facilities at ARL Penn State
6. Acquisition and installation of TAES and other advanced VOC destruction technologies as appropriate at (MC)<sup>3</sup> Albany (USMC funds)
7. Evaluation of pollution prevention options for (MC)<sup>3</sup> degreasing operations.

The following activities will run continuously after completion of the first five tasks:

1. Data collection and analysis at (MC)<sup>3</sup> Barstow, ARL Penn State, and EPA
2. Implementation of optimization technologies on (MC)<sup>3</sup> Barstow APCS
3. Feedback to TAES and EPA for future system improvement
4. Interface with California Air Resources Board (CARB) and Georgia EPD
5. Publication and dissemination of results by all appropriate means

Technical issues to overcome:

While no single issue threatens the success of this program, four main technical issues will determine the degree of success:

1. Extent to which recirculation/partitioning can be applied without exceeding OSHA limits or violating NFPA codes (affects flow rate to control system and; therefore, the size and costs of the system)

2. Individual and collective efficiencies of the three components of the Terr-Aqua control system (UV, wet scrubber, carbon adsorber)
3. Potential for conversion of incoming VOCs to other compounds in the control system
4. Multimedia impacts of alternative approaches for solvent cleaning.

#### **Expected Payoff:**

The immediate benefits of this program will be accrued by (MC)<sup>3</sup> Barstow and, subsequently, by (MC)<sup>3</sup> Albany. An aggressive technology transfer effort will ensure that any DoD or private facility which uses spray paint booths or vapor degreasing tanks can derive benefits from this program well before its completion.

The program will enable the (MC)<sup>3</sup>'s and numerous other DoD facilities to continue to accomplish their mission while complying with federal, state, and local air quality regulations. Additionally, the resulting technology transfer will ensure the availability of systems to private industry which may, in the extreme, keep them in business, help them continue to operate within the US, or, at a minimum, reduce their negative impact on the environment. The facilities and equipment which are purchased or enhanced under this program will be available for additional R&D efforts after program conclusion.

The (MC)<sup>3</sup>'s perform the depot level maintenance on all of the equipment deployed aboard the Maritime Preposition Fleet (MPS) ships. The importance of this effort is seldom more obvious than now, as we watch the Marines deploy the equipment in Somalia. It is essential that we sustain the complete array of capabilities vital to the MPS equipment maintenance at our two U.S. Marine Corps Depots. Painting and cleaning are links in the maintenance chain which need immediate attention, and which will respond most quickly to the inspection of new technologies.

#### **Milestones:**

Design a recirculation spray booth at (MC)<sup>3</sup> Barstow

Acquire and install new TAES APCS at (MC)<sup>3</sup> Barstow (USMC funds)

Acquire and install additional laboratory equipment necessary for R&D at ARL Penn State

Initiate data collection process at (MC)<sup>3</sup> Barstow and correlation process with research at ARL Penn State and EPA

Complete inventory of MC<sup>3</sup> Barstow VOC emissions

#### **Funding: (\$K)**

		SERDP	Other Contributing Research
FY93	(MC) <sup>3</sup> -	1000	1250
	EPA -	1750	1000
	Total -	2750	2250*
FY-94	(MC) <sup>3</sup> -	1000	1250
	EPA -	1750	1000
	Total -	2750	2250*

\* The USMC will purchase the full scale APCS with non-SERDP funds and EPA has ongoing pollution prevention research which will support the goals of this research proposal.

It is the intention of all the partners in this project that the funding be provided directly to (MC)<sup>3</sup> and EPA as shown above. A coordinating committee chaired by the U.S. Marine Corps will be set up to coordinate all activities under this program.

**Transition Plan:** Work accomplished under this funding is intended to provide information on the performance and cost of innovative emission reduction approaches for VOCs and air toxics which will be commercialized by private vendors for use at other military installations and private sector companies with similar operations. (MC)<sup>3</sup> Albany, GA and (MC)<sup>3</sup> Barstow, CA will be available as beta sites for the improved APCS, modified spray booths, and pollution prevention approaches. TAES is envisioned as the commercialization partner for the APCS. The desired end result is affordable, commercially available equipment and systems which facilitate vapor degreasing, painting, and paint removal with no loss of efficiency, and which comply with air emission quality standards.

**Performers:**

The (MC)<sup>3</sup> and the EPA will execute this program as a team. ARL Penn State will be the major technical contributor to the Marine Corps effort.

**Technical Points of Contact:**

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**SERDP Thrust Area: Pollution Prevention**

**Title:** Alternatives to Halon 1301 for Ground Vehicle Crew Compartments

**Problem Statement:**

This program addresses replacement of Halon 1301 in manned spaces of ground combat vehicles with an environmentally safe alternative. The Army uses less than 1 percent of national Halon consumption.

**Project Description:**

Under provisions of the Montreal Protocol and Clean Air Act of 1990, production of Halons and other ozone depleting chemicals (ODC) will stop. DoD 6050.9 and AMCR 70-68 mandate phaseout of ODC use. An alternate agent must be identified to support fielded and future weapon systems. Path I will "fast-track" two most promising agents that have majority of toxicology testing completed, aimed at finding an agent by the end of FY 96. Path II is a concurrent, longer term, lower risk, evaluation of multiple agents as backup in case an acceptable agent is not found on Path I tests.

**Milestones:**

	PATH I	PATH II
Candidate identifications	2QFY93	3QFY94
Toxicology profiles	3QFY93	4QFY94
Agent performance testing	4QFY95	4QFY97
Toxicology studies	4QFY96	4QFY99
Agent selection	4QFY96	2QFY00

**Funding: (\$K)**

	FY93	FY94
SERDP	1524	5175
Service Funds	1375	4655

**Performers:**

TACOM, TECOM and AEHA.



**Technical Point of Contact:**

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\* Note: The SERDP Scientific Advisory Board provided specific guidance to this project. Their position statement on this effort may be found in a separate section within this document; see "Table of Contents."

## **SERDP Thrust Area: Pollution Prevention**

**Title:** Evaluate Replacements for Ozone Depleting Substances (ODSs) used in Military related Refrigeration Systems and Disposal of ODSs

### **Problem Statement:**

The goal is to assist the DoD to evaluate, test, and select the optimal alternative compounds and systems for refrigeration related uses of ODSs which are now contributing to the stratospheric ozone depletion problem and to provide for safe ODS disposal. EPA will target those uses in the military which we know will benefit the most from the experience of the scientists and engineers in the Stratospheric Ozone Protection Branch of the Air and Energy Engineering Research Laboratory (AEERL). The research conducted will emphasize alternative approaches which minimize other environmental impacts such as global warming.

This proposal is an augmentation to a Phase I SERDP project to evaluate HFC-236ea as replacement for CFC-114 now used in Navy shipboard chillers. The U. S. Navy has established a proactive schedule to eliminate all ozone-depleting CFC refrigerants from its fleet beginning in 1996. Approximately 950 shipboard centrifugal compressor air-conditioning plants ranging in capacity from 125 to 360 tons of cooling per unit are in use currently. CFC-114 has been the refrigerant of choice for this application since the early 1970's but is to be completely phased out of production by January 1, 1996. The EPA's AEERL has discussed the merits of HFC-236ea with the Naval Surface Warfare Center (NSWC) and both parties have agreed to further evaluate the use of HFC-236ea as a possible alternative to retrofit the Navy's shipboard CFC-114 chillers. This proposal would provide funds to augment the performance evaluation and initiate nonchronic toxicity tests on HFC-236ea for the purpose of obtaining TSCA listing to allow commercial use.

This proposal is an enhancement to a project funded under Phase I of SERDP.

### **Project Description:**

The NSWC has established a research program to "identify or develop alternate processes, chemicals, or techniques for functions currently being met by CFCs and halons." HCFC-124 is now being investigated by NSWC as a possible alternative refrigerant to retrofit existing shipboard CFC-114 chillers. However, even if this chemical should prove acceptable for use in existing equipment, it too will eventually be phased out of production as an ozone-depleting compound. As stated above, EPA under SERDP has initiated research to evaluate HFC-236ea as a replacement for CFC-114.

Clearly, a better alternative than HCFC-124 would be one which could substitute for CFC-114 with little or no equipment modifications, perform to Navy specifications, and not be subject to production restrictions. HFC-236ea is a compound which appears to meet all of those qualifications. However, HFC-236ea is not now commercially available so that a very stringent timetable of testing and evaluation must be performed to bring it to commercial use within the Navy's schedule. AEERL has already acquired sufficient thermophysical property data to model the performance of the new chemical as a CFC-114 replacement. Results of the modelling suggest that the compound could serve as a near "drop-in" substitute for CFC-

114. AEERL has also conducted tests which show the chemical to be nonflammable, thermally and chemically stable, compatible for use with common chiller materials, and miscible with polyolester lubricants. Toxicity tests with rats at a relatively low exposure concentration (ca. 1000 ppm) have shown the chemical to be nontoxic at that level. AEERL is now sponsoring further work with HFC-236ea including measurement of heat transfer coefficients, sonic velocities, ideal gas heat capacities, and an extended array materials compatibility tests.

The objective of this program is to augment the ongoing performance testing and perform necessary toxicity evaluations to enable the compound to be produced for commercial use.

In order to produce and sell a chemical on the commercial market, the chemical must be "TSCA-listed", which is to say that the chemical must have passed a battery of toxicity evaluations to ensure that the chemical is sufficiently safe to produce, handle, transport, and use for the intended application. Thus, the required toxicity tests must be accomplished in a very short timeframe in order for HFC-236ea to be available for retrofitting Navy chillers should the new chemical be deemed suitable from a performance standpoint.

The subject proposal will allow procurement of an additional quantity of chemical sufficient to perform the necessary toxicity tests to enable the chemical to be "TSCA-listed" and produced for commercial sale. These toxicity tests include determination of an acute inhalation toxicity ( $LC_{50}$ ), cardiac sensitivity threshold, sub-acute inhalation toxicity, genotoxicity, and developmental toxicity. Approximately 2330 pounds of chemical and one year will be needed to perform these tests.

The tasks to be conducted are to (1) procure sufficient quantities of sufficient purity of HFC-236ea and (2) perform the desired toxicity tests. A supplier willing to supply approximately 1000 pounds of the chemical is currently being sought to meet the needs of the performance test program including testing the chemical in a full-size CFC-114 chiller but not including toxicity testing.

This work directly supports the goals of Pillar 3 (pollution prevention) in the Tri-Source Research Plan which has a goal to eliminate the need to purchase ozone depleting substances by the end of 1995. In particular it supports works under thrust 3F to identify safe, affordable chemical substitutes for ODS refrigerants and re-engineer existing shipboard and shoreside plants for use with new non-ODS refrigerants.

#### **Expected Payoff:**

This application has wide potential use in all the services as well as general wide use in the public sector (e.g., chillers for building cooling and supermarket refrigeration).

This project will benefit DoD and the public to various degrees. Replacements for CFC-114 refrigeration uses will eliminate uses of an ozone depleting chemical, and the replacement will have minimal environmental impact. Success will allow a one time design change for the Navy chillers rather than an interim solution followed by a permanent solution. The disposal work will allow destruction of remaining unneeded ODSs which will prevent further destruction of the stratospheric ozone layer.

**Milestones:**

Times are from an assumed contract award in 9 months.

Procure needed quantities of chemical	12 months
Complete toxicity tests	30 months

**Transition Plan:**

Results would be reported to NSWC for incorporation into the more complete evaluation being performed on HFC-236ea. The Navy will be part of the decision process on tests and informed as results are received.

**Funding: (\$K)**

FY93  
300

Related: Phase I SERDP was 500K; EPA CFC-114 work is about 100K/year

**Performers:**

The primaries are Air and Energy Engineering Research Laboratory, EPA, RTP, NC with contracts to testing laboratories and chemical manufacturers. Naval Surface Warfare Center would be part of the team to decide on specific tests to meet their needs.

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Propellant Recycling**

#### **Problem Statement:**

The goal of this project is to develop and demonstrate methods for recycling double base propellant scrap. One double base propellant was chosen as the focal point for the recycling effort, the AA2 propellant which is processed into the MK 90 propellant grain or the MK 66 missile. An evaluation of the applicability of the work on this propellant to other double base extruded propellants will be investigated.

The pollution prevention techniques developed by this program will be most applicable to Navy and Army ordnance production facilities and their contractors, but can also be used by Air Force production facilities involved in the double base manufacturing business.

Prior to the start of this project, press necks (chunks of scrap propellant) and reject grains have successfully been returned to the supplier for recycling for some double base propellant. It was believed that there was a potential to recycle any uncontaminated double base propellant. The studies were initiated and completed. These studies have confirmed the ability to rework up to 20 percent of uncontaminated propellant from any scrap generation point. It may also be possible to rework scrap propellant containing small amounts of ethyl cellulose into grains with negligible effects on the burn characteristics of the propellant. Other options which had not been investigated thoroughly for using scrap propellant are several uses as mining explosives. Initial samples have been provided to industry for testing as a bulk explosive. Although the samples provided did not meet the needed size requirement for their current pumping equipment, the propellant seemed to perform adequately to be substituted for ammonium nitrate and indicated an increase in energetic capacity during detonation.

The increasing focus on toxic air pollutants emitted into the environment by industry has placed an additional emphasis on the reduction of double base propellant scrap. Current practice for disposal of scrap propellants and explosives is through open burning/open detonation of scrap. Many double base propellants contain ballistic modifiers which have heavy metal components. These heavy metal components combine with oxygen when burned to create toxic air pollutants. New Clean Air Act Amendments are requiring tighter controls on burning of toxic constituents. Specifically, open burn/open detonation is not expected to be permissible after the year 2000. States are also tightening their requirements on the incineration of toxic materials.

#### **Project Description:**

The objective of this effort is to determine alternative product uses for double base propellant as opposed to disposal via incineration or OB/OD. An analysis of the factors affecting each option will be included.

The technical approach for this project is to (1) investigate the feasibility of reblocking the scrap double base propellant into smaller double base grains to be used by the fleet, (2)

demonstrate and outline requirements for the use of double base scrap as rework in virgin material, and (3) investigate and outline requirements for the use of double base scrap as a mining explosive.

There are several tasks that must be completed to accomplish the proposed project. These are (1) determine size requirements for ground propellant; (2) survey processing equipment for best suited equipment; (3) perform sample granulations of propellant; (4) provide granulated propellant to mining explosive plants for evaluation; (5) provide granulated propellant to pilot plant for rolling with virgin propellant; (6) develop sample booster charge for granulated propellant; (7) summarize results; and (8) transference to production.

This project will assist in the Navy's objective to reduce its generation of hazardous waste by 50 percent. The Army has a similar hazardous waste minimization objective, although the baselines may differ. Additionally, the DoD's blanket exemption of OB/OD for the destruction of scrap ordnance material is coming under increasing scrutiny by the various regulatory agencies. It is widespread belief that, at a minimum, limits will be set for the treatment of scrap propellant and explosive. The investigation of alternative uses for the scrap propellant is a proactive way of minimizing the explosive hazardous waste generation before the regulatory agencies require minimization.

There have been no DoD efforts to research other uses for scrap double base propellant. Hercules, at the Sunflower Army Ammunition Plant, had completed some studies of reworking contaminated double base propellant into virgin material; however, many technical questions such as the effect on the ballistic properties of the reworked material and particle size effects on the rework were not included. Other private contractors have completed or are currently recycling components of cast propellants; however, the components are entirely different and the findings cannot be related to double base propellants.

Although it has long been acknowledged that uncontaminated rework into the double base propellant will not harm the propellant and in fact may help some of the mechanical properties, the extent to which small amounts of inert material can be accommodated is relatively unknown. Initial work completed on this project shows that the technology of using double base propellant as a mining explosive or as rework has a very low risk.

#### **Expected Payoff:**

It has been confirmed that a market exists for the scrap double base propellant if the propellant can be reduced to an acceptable particle size. Capital costs for equipment are estimated to be a maximum of \$100K. If the ground propellant can be used as rework in a propellant motor, each pound will replace a pound of virgin material at a cost of \$9 per pound. If the ground propellant can be used as a bulk explosive, industry may reimburse us with a cost of \$0.10 per pound. If the ground propellant can be used as a booster charge, the propellant can be sold for \$1 per pound. At a double base scrap production rate of 300,000 pounds per year for a single facility, a simplified look at the economics reveals a payback period of 3 years for propellant used as a bulk explosive (worst case).

**Milestones:**

Tasks 1 through 7, mentioned earlier, are expected to be completed during FY93. Continuous contact is being kept with the production facility. With the successful completion of this project, all equipment specifications will be completed and all industrial contacts made. The production facility will only need to determine if the recycling effort is economically feasible and order and install the specified equipment.

**Transition Plan:**

Upon the completion of this project, the findings will allow the production facilities to immediately adopt the technology.

**Funding: (\$K)**

FY93  
100

**Performers:**

NSWC/Indian Head Division and ICI Explosives. In addition, we are currently in contact with the largest mining explosive production facility in the United States and are entering into a cooperative agreement to investigate new business opportunities. The pilot plant has completed all necessary engineering needed to perform the rework of contaminated propellant into virgin material; however, they are having operating problems with some of their equipment. The completion of this phase of the project is dependent upon the equipment operating properly.

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**SERDP Thrust Area: Pollution Prevention**

**Title:** Elimination of Lead and Antimony Compounds in Solid Film Lubricants (mL-L-46147)

**Problem Statement:**

The solid film, air-cured, corrosion-inhibiting, lubricant MIL-L-46147 is currently permitted for use to meet performance requirements although it contains lead and antimony compounds. These compounds adversely affect the environment. A reformulation effort could result in the elimination of these environmentally objectionable compounds without loss of performance.

Prohibition of lead-containing lubricants and chlorofluorocarbon propellants is anticipated by regulatory action. This project will develop replacement formulations ahead of time to allow continuity of supplies during transition to environmentally compliant lubricants.

**Project Description:**

The program objective is to evaluate candidate formulations and assess performance properties. Storage and sprayability tests with alternate propellants for aerosol cans will also be conducted as well as limited field tests of typical applications. Technology is believed to be available, but unproven for military use.

**Milestones:**

	Completion Dates
Test candidate formulations	FY 93
Complete testing, prepare specification draft	FY 94
Conduct limited field test	FY 95

**Funding: (\$K)**

	FY93	FY94
SERDP	100	100
Service Funds	110	100

**Performers:**

BRDEC—James Mengenhauser (703) 704-3733

Proposed Technology Customer(s): Defense General Supply Center (DGSC) is the procuring agency and buys for all DoD customers.

Mode of Implementation: Revise MIL-L-46147 and qualify environmentally compliant products.



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## **SERDP Thrust Area: Pollution Prevention**

**Title:** An Environmental Knowledge-Based Advisor for Facilities Life Cycle Decisions

### **Problem Statement:**

The goal of this project is to develop and field test a knowledge-based model of environmental characteristics/attributes to support the decision processes involved in facility design, construction, and operation.

Decisions (i.e., design, construction, operation and renovations, and demolition) are made throughout a facility's life cycle which are based primarily on economic and in-place performance. Environmental factors (e.g., energy and resource use, toxic by-products, indoor air quality, siting, waste products, etc.) are not considered in any of the current technical, pricing, or planning data used as the basis for these decision. The inclusion of environmental factors are essential in optimizing the standard facility decision processes, obtaining the maximum benefits from limited natural and economic resources, and reducing the potential for adverse environmental impacts.

This project is an enhancement of an existing US Army's Corp of Engineers' Construction Research Laboratories (CERL) Small Business Innovative Research effort to test the feasibility of a Knowledge-Based Model which combines environmental and the standard facility decision factors. CERL FY92 funds for this project were \$50K. Joint funding in FY93 and FY94 from the Corp of Engineers is expected but not finalized.

### **Project Description:**

The US Army's Corps of Engineers' Construction Research Laboratories (CERL) are currently exploring the feasibility of a Knowledge-based Model that will enable the consideration of environmental factors during the various phases of a facility's life. In addition, CERL performs research to improve and optimize the various components (e.g., costs, system performance, etc.) of facility construction and operations and to improve construction productivity.

AEERL's Indoor Air Branch (IAB) is involved in research to characterize indoor emission sources and methods of mitigating indoor air quality (IAQ) impacts. IAB has a cooperative agreement with the American Institute of Architects (AIA) to develop environmental life cycle data for materials used in construction. IAB is finalizing a set of catalogs on indoor air emissions sources which assigns SIC Codes, MasterSpec Codes, chemical constituent, and chemical emissions data to those materials typically found in indoor environments. IAB has also completed a data base of emissions factors for those materials identified as potential indoor air sources.

The proposed project will utilize AEERL's experience in materials life cycle and indoor environments and CERL research experience in facility design, construction and operation to expand, enhance and field test CERL's Knowledge-Based Model prototype.

The technical approach will include the following components:

- 1) Expansion of the existing model to include additional data sets;
- 2) Expansion of CERL data on facilities such as the performance and costs of various systems;
- 3) Inclusion of IAB's Indoor Air Exposure model and emissions data;
- 4) Modification of AIA/IAB's Life Cycle Methodology;
- 5) Expansion of the cataloging activity to include all construction materials;
- 6) Data gathering from primary sources;
- 7) Model validation.

This project will require close coordination between the sponsoring agencies, facilities managers, designers, general contractors, manufacturers and IAQ experts.

DoD is potentially the single largest builder and manager of facilities in the world. The proposed Knowledge-Based Model will help DoD to optimize environmental and economic considerations over the life of these facilities.

This project is directly related to DoD/DOE's Pillar 3-Pollution Prevention; Thrust 3.J.: Life cycle Environmental Assessments; item (3.III.2.d): Environmental life cycle cost model. It compliments on-going IAB research in IA emissions and control technology characterization and modified materials life cycle assessments. It also enables CERL to move from its prototype knowledge base to a full-scale, marketable decision making tool.

The AIA is currently working with IAB to compile information on the environmental impacts of selected materials which can be used by design architects. This information will be made available to the users in an electronic format.

There is no existing comparable effort to bring together such a broad array of environmental and construction data into a single expert system which will be available to such a broad range of users.

Tasks for project completion include:

- 1) Incorporation of IAQ Exposure Model;
- 2) Beta Test of expanded knowledge base model
- 3) Acquisition/development of pertinent data sets
- 4) Development of pre-production knowledge based model
- 5) Optimization and beta test of model
- 6) General Distribution

Technical issues to overcome involve the restructure of the prototype model to include IAQ components, expansion of the model to accommodate the CERL and IAB data sets, acquisition and development of new data, quality assurance, and optimization of final knowledge base.

#### **Expected Payoff:**

The Users include architects, engineers (e.g. HVAC engineers), facilities designers, construction managers, public agencies (e.g., GSA, Corp of Engineers, etc.), state and federal policy makers, and materials manufacturers.

The model will promote environmentally-sensitive decision making throughout a facilities life cycle. The impacts of this approach to decision making to the various components of the life cycle include the following:

**Building materials' and equipment manufacture:**

- Reduced negative impact on resource consumption;
- Reduced undesirable manufacturing by-products;
- Reduced exposure to hazard (e.g., IA contaminants).

**Construction:**

- Reduced undesirable waste in terms of quantity and content;
- Reduced pollution generating activities;
- Reduced human exposure to hazard

**Operation and Maintenance:**

- Reduced operating expenses; energy, and resource consumption;
- Improved service life
- Reduced undesirable wastes
- Reduced exposure to hazards (e.g., IAQ impacted from cleaning activities)

**Disposal:**

- Reduced waste and enhanced opportunities for recycle.

**Milestones:**

Complete Phase I Environmental Knowledge Base Model	5/93
Initiate Phase II Pre-production Model Development	7/93
Complete Phase II Model	7/95
Initiate Phase III Model Beta testing	8/95
Release to Public	8/96

**Transition Plan:**

Successful Tech Transfer involves a strong marketing entity, capable of effective implementation in practice and/or a commercial method that sells itself by virtue of its quality and utility. The integration of this product by the Corp of Engineers, DoD, and GSA into its decision matrix for new and existing facilities will act as a driver for the broader usage.

**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
CERL	150	150
EPA	295	300
EPA SERDP	500	300

\*EPA Funding for FY93-FY94 were spent to develop AIA/EPA's LCA materials methodology. In addition, AEERL has spent an estimated \$1.050K in the development of the

components necessary to this model's success. These expenditures were as follows: \$300K in the development of a LCA materials methodology; \$375K for developing materials catalogs; \$75K in the development of IA emissions data base; and \$300K in the development of IAQ models.

**Performers:**

Air and Energy Engineering Research Laboratory  
US Army Corp of Engineers/CERL

**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Alternate Solvents for Propellant Manufacture**

#### **Problem Statement:**

Solvent type propellants are manufactured using volatile organic solvents. For those solvent type propellants containing nitroglycerin (NG), the solvents are lost to the atmosphere as volatile organic compounds (VOCs). Technology to capture these VOCs in the presence of NG is not currently available. Emission standards for these VOCs continue to be more restrictive. Even if technology is developed, operational costs may be prohibitive. The objective is to investigate the substitution of solvents of low volatility to prevent the pollution.

The project is expected to prevent violation of pollution standards for the release of volatile organics to the atmosphere while allowing the recovery and reuse of the solvents.

Targeted organizations include those using propellants manufactured by the solvent process. It may be viable also for some propellants not made by the solvent process.

#### **Project Description:**

Industry is continuing to evaluate new low volatility solvents to comply with VOC emission standards. Compounds such as diacetone alcohol and other dibasic ester solvents are being evaluated. In this project, the technical feasibility of using less volatile solvents in place of acetone, ethyl alcohol and diethyl ether will be determined.

Multi-base propellant manufacture requires mixtures of acetone and ethyl alcohol while single-base propellants require mixtures of ethyl alcohol and diethyl ether. Mixture of less volatile solvents may also be appropriate solvents. The approach for this determination is to evaluate new solvent systems based on pressure, costs, and compatibility with the solvent removal and recovery system. End item testing will then be accomplished on propellants made with alternate solvents. This is a new project.

#### **Transition Plan:**

Final report will provide implementation recommendations and design data for follow-on ballistic testing and in-process modifications to be done under facility projects.

#### **Milestones:**

##### **Phase I**

	Completion Dates
Funding Authorized	2Q FY 93
Literature Search and Toxicity Assessment	2Q FY 93
Laboratory Evaluation	4Q FY 93
Interim Report	4Q FY 93
Pilot Extrusion Studies	2Q FY 94
Develop Operating Parameters	3Q FY 94

Design Data  
Final Report

4Q FY 94  
4Q FY 94

**Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
SERDP	210	240
Service Funds	45	45

**Performer:**

Radford Army Ammunition Plant/ARDEC

Proposed Technology Customers include all solvent propellant manufacturing facilities.  
Currently, RAAP.

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Solventless Pyrotechnic Manufacturing**

#### **Problem Statement:**

The goal of the proposed work is a field demonstration of the cryogenic processing technique as a solventless method to eliminate toxic air pollutants (TAP) and volatile organic compounds (VOC) emissions from the Magnesium-Teflon-Viton (MTV) pyrotechnics manufacturing process. Once the demonstration is complete, similar pyrotechnic processes can be improved using this technology.

This project will encompass a great portion of the pyrotechnic processing that DoD is engaged in. MTV and similar pyrotechnics are used in igniter compositions and IR flare decoys by all branches of the Armed Services.

MTV is currently manufactured using a crash precipitation method called the "shock-gel" process. Although the process is extremely effective in coating the magnesium and Teflon, it is a hazardous process that generates large amounts of hazardous waste and constantly releases VOC's And TAP's to the environment.

The "shock-gel" process is a lengthy batch process which requires a large quantity of solvent (acetone and hexane) to effectively coat the magnesium and Teflon with the Viton binder. The process begins by dissolving the Viton binder in acetone. Magnesium and Teflon powders are then added to the solution and mixed. Once the solids are properly dispersed throughout the mix, the mixture is shocked with hexane to precipitate the binder out of solution onto the solid particles. The solvent is then decanted from the mixture and the procedure is repeated to ensure that all the remaining acetone is washed from the pyrotechnic. The solvent wet powder is manually transferred to an oven and dried to drive off the remaining volatiles. At this point the MTV powder is ready to be consolidated into its final form. The collected solvent must be disposed of as hazardous waste due to the toxic nature of the solvents. It takes five 55 gallon drums of solvent to process 200 lbs of MTV at NSW, IHD. Not only are these solvents expensive to purchase, ranging from 1 to 3 dollars per gallon, they are quite costly to dispose of. The current cost of disposing of hazardous waste is 600 dollars per 55 gallon drum. This represents 11 percent of the total MTV production cost, and it is projected that disposal costs will increase as the environmental regulations tighten. The Clean Air Act Amendments of 1990 requires that air toxic emissions be reduced by over 75 percent in the next ten years using the maximum achievable control technology (MACT). Hexane is specifically listed by the EPA as an air toxic and therefore emissions must be reduced. In addition to the air toxic emission requirements, the Clean Air Act also regulates the emissions of volatile organic compounds (VOCs). Both acetone and hexane are VOCs. Under the new law, areas which are classified as nonattainment will be required to reduce the VOC emissions by 3 percent each year until the new national ambient air quality standard (NAAQS) is met. For large pyrotechnic plants or multiple product energetic facilities such as IHD,NSWC emissions from the "shock-gel" process will have to be reduced. In order to use the "shock-gel" process in the coming decade, expensive filters and vapor recovery systems will have to be installed and maintained. Compliance with the Clean Air Act Amendments of 1990 will result in increasing the manufacturing costs of



pyrotechnics produced by the "shock-gel" process and will limit the number of manufacturers.

Not only do these solvents create many environmental hazards, they are a major factor in the explosive safety hazards associated with the process. Incidents involving accidental ignition of MTV have been reported in every stage of the manufacturing process from mixing to pressing. Results of such accidents range from loss of material and equipment to loss of life and facilities. Mixing, handling and even consolidation can generate electrostatic charges in and on the MTV pyrotechnic. Because of its low resistivity, these charges can build up to dangerously high levels, eventually producing an electrostatic spark. Highly flammable solvent-air mixtures present in and around the pyrotechnic mixture during each step of the process compound the hazard. These solvent-air mixtures require much less energy for ignition than the pyrotechnic compositions and produce flames above the materials auto ignition temperature. If the concentration of the solvent in air is within the flammability limits, then the gaseous mixture can ignite, leading to ignition of the entire pyrotechnic composition.

The obvious solution to all the processing problems associated with the "shock-gel" process is to eliminate the solvents. Immediately, you come into compliance with the Clean Air Act Amendments of 1990 and at the same time dramatically improve the safety of the process. The cryogenic process for manufacturing MTV is a solventless process that has been demonstrated on a small scale. In the cryogenic process the Viton is cryogenically ground to a fine particle size using inert liquid nitrogen (LIN). The ground Viton is collected in LIN to inhibit particle agglomerations. The ground Viton is warmed to 0°F and classified to less than 150 microns. The Viton is weighed at the elevated temperature and then the magnesium Teflon, and Viton are then chilled to LIN temperatures. Once the ingredients have reached equilibrium, they are mixed in a slurry of LIN at a relatively low solids loading approximately 30 percent. When a uniform distribution of the ingredients has been attained, the temperature of the slurry is increased and the LIN is vaporized. Because of the extremely low boiling point of LIN(-320°F at 1 atm), this process can be accomplished at ambient temperature without an external heat source. Once the LIN has vaporized, the relatively free flowing pyrotechnic powder can be pressed or extruded into the appropriate size and shape using conventional molding technology.

The advantages of the cryogenic process are overwhelming. Due to the reduced number of processing steps utilized in the cryogenic approach, the explosive operators are exposed to fewer hazardous situations compared to the current process. Using a solventless process to manufacture MTV eliminates the solvent disposal cost. Additionally, the potential for an accidental ignition during the process is reduced to the sensitivity of pyrotechnic alone and not compounded by the solvents. In terms of environmental liabilities, there are none. Nitrogen is an environmentally benign gas that makes up 79 percent of the air we breathe, every day.

#### **Project Description:**

The objective of this proposed effort is to demonstrate the use of cryogenic processing on the pilot scale as a method of eliminating the hazardous waste and harmful emissions caused by the solvents used in the manufacture of magnesium-TeflonViton and similar pyrotechnic

materials. The field demonstration will be at a DoD site.

The technical approach proposed to demonstrate the solventless manufacture of pyrotechnics on a production scale is to (1) identify a suitable method to classify the particle size of cryogenically ground Viton, and develop material handling techniques necessary to process the extremely cold material in a moisture free state, (2) install a pilot scale cryogenic processing facility and optimize the process parameters necessary to manufacture quality MTV, and (3) assuming success transition our "shock-gel" production process to a cryogenic process and begin processing other energetic materials manufactured by the "shock-gel" process.

The tasks required to accomplish the proposed project are outlined below.

1. Complete the installation of cryogenic grind equipment.
2. Issue contract for liquid nitrogen
3. Debug and start up grinding equipment.
4. Contact private industry and identify candidate particle size classifiers.
5. Evaluate each particle size classifier and select the most suitable.
6. Procure particle size classifier
7. Install and debug particle size classifier.
8. Grind Viton on pilot scale.
9. Manufacture small scale (3-20 lbs) batches of MTV.
10. Extrude and Test MTV.
11. Program Evaluation/Progress Report

The objectives of this effort are directly related to many DoD programs designed to reduce harmful air emissions, to minimize hazardous waste and comply with all federal legislations as described in OPNAVINST 5090.1A' "Environmental and Natural Resource Program Manual."

For the last three years, NSWC, IHD was involved in a joint program with the U.S. Army Armament Research, Development & Engineering Center (ARDEC) to investigate the possibility of using a cryogenic processing technique to manufacture MTV and other magnesium-Teflon based pyrotechnics. The program resulted in demonstrating the feasibility and comparability of cryogenic MTV to current production systems. It also identified several processing problems that must be resolved before a production process can be developed. This proposed effort would continue the efforts of the joint program and continue to share information with the Army.

We have identified several hazards associated with the cryogenic manufacture of MTV. During the mixing process, alarming quantities of static electricity were measured. If the static electricity were discharged into the pyrotechnic composition, it could result in an ignition. In order to reduce the static electricity to safe levels, we have had to add 1/2 percent by weight acetylene black to the composition. This has not affected the performance of the MTV in an igniter system; however, questions have been raised about the possible negative effects on flare compositions. Grinding the Viton binder to a sufficiently small particle size is critical. If the binder is not adequately reduced, the MTV does not consolidate properly in the press. A method of controlling the particle size of the ground binder has not

been identified. The previous work on this project successfully demonstrated the technology using small scale unsophisticated equipment and approaches.

#### **Expected Payoff:**

The Army has estimated a potential cost savings of \$900,000.00 if their current 600,000 lbs per year "shock-gel" production process for flare decoys were replaced with the cryogenic process. Other benefits are realized in the area of environmental compliance. The elimination of waste streams from any process benefits the production facility by eliminating the need to install expensive pollution abatement and treatment systems.

#### **Milestones:**

Project accomplishments during FY-93: The expected accomplishment for FY 93 are tasks 1 through 6 as outlined above. The equipment will be installed at NSWC,IHD. The previous program has enhanced the Division's ability to process energetic materials cryogenically. A chart projecting the tasks and milestones for the entire project is presented below.

#### **Transition Plan:**

The design and construction of a production facility for processing MTV cryogenically will be based on the success of the proposed project. The production requirements for MTV at the NSWC,IHD are 2000 lbs/yr. This will enable the Division to use the equipment as a test bed to improve other pyrotechnic manufacturing processes by applying the cryogenic approach. The results from these tests, will be made available to those facilities processing the specific items, and the technology will be transferred if they are interested.

As the work progresses on the proposed project, information will be freely exchanged with those organizations currently in the business of producing magnesium-Teflon based compositions, such as the ARMY.

To date all the equipment used in the cryogenic process has been standard production equipment commonly found in energetic processing facilities. Liquid nitrogen is handled in industry standard dewars and tanks.

#### **Funding: (\$K)**

FY93  
355

#### **Performers:**

Naval Surface Warfare Center, Indian Head Division

To date this program has drawn heavily upon the expertise of manufacturers of cryogenic grinding equipment and cryogenic grinding companies to develop feasible approaches for reducing the size of the Viton Co-polymer. Some services were provided free of charge and others were contracted. This cooperative approach with private industry will be extremely

useful in identifying an acceptable particle classification system which is critical for the advancement of this technology.

Based on the previous work, the Army is planning to develop a cryogenic process to manufacture MagnesiumTeflon-Hytemp. We have agreed to exchange information and data in order to avoid repetition of work. This exchange of information will be strictly informal. It is hoped that we can exchange services to compliment each others program.

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Extraction & Recycling of LOVA Propellants Using Supercritical Fluids**

#### **Problem Statement:**

Solid gun propellants are currently destroyed by open pit burning or incineration; supercritical fluid (SF) recycling, rather than destruction, would have both economic and environmental advantages. Unfortunately, propellant ingredients have insufficient solubility in non-reactive SCFs (e.g., CO<sub>2</sub>). The objective of this new program is to identify suitable SF solvents for use in extracting and recycling the ingredients of solid "LOVA" (low vulnerability ammunition) gun propellants being developed for AMC munitions development programs. This is a SERDP Phase 1 funded project.

#### **Project Description:**

Supercritical fluids (SF's) have two potential environmental-related applications related energetic materials demilitarization: destruction via oxidation in SF's (HAZMAT destruction), and "solventless" SF extraction/separation for purposes of recycling (pollution prevention). The first area is being actively pursued (see C&E News, Dec. 23, 1991): the DoD has established a pilot plant that uses supercritical water to destroy military toxic wastes. For the long term, however, recycling should be the preferred approach. There is a fundamental dilemma, however: While the energetic materials, polymeric binders, and other ingredients of solid propellants tend to be highly soluble in the (polar) SF solvents used for destructive oxidation (e.g., supercritical H<sub>2</sub>O, T<sub>c</sub>=374 °C), the solubilities in "Inert" solvents (e.g., supercritical CO<sub>2</sub>, T<sub>c</sub>=31 °C) that one would like to use for extraction/recycling are too low for the process to be economically feasible.

The research involves experimental and theoretical investigations of the effectiveness of polar "modifiers" in increasing the solubility of energetic materials (e.g., HMX, RDX) and binder components in supercritical CO<sub>2</sub>. The goal will be the identification of polar "modifiers" that (a) significantly increase solubility of the solid propellant components in SF CO<sub>2</sub>, (b) do not result in hydrolysis or other chemical degradation of the propellant ingredients, and (c) can either themselves be recycled (SF extractors can operate closed-cycle), or are as close as possible to neat CO<sub>2</sub> in having negligible environmental impact. In addition to polar modifiers, several alternative (to CO<sub>2</sub>) supercritical solvents have been identified and will also be investigated; these are fluids with significant dipole moments, but that are not ozone-depleters.

For other systems/applications, CO<sub>2</sub> modifiers at the 1-5 percent level have increased solubilities by up to several hundred percent.<sup>1</sup> This research is probing the relationship between modifier molecular structure and its effect on solubility of nitramine energetic materials and other propellant ingredients. The research also involves finding the optimum SF conditions (e.g., temperature, pressure/density) for promising CO<sub>2</sub>-polar modifier supercritical solvents.

The experimental work involves measurement of nitramine (and other ingredient) solubilities in supercritical solvents using a variety of polar modifiers, and under several supercritical

conditions (e.g., both close to- and far from- the critical point). Two experimental techniques are being used to measure solubility. One involves spectroscopic detection using an optical (windowed) supercritical cell; the other involves use of a supercritical fluid extractor (SFE) interfaced to a supercritical fluid chromatograph (SFC).

The theoretical work serves to guide the experimental effort: theoretical solubility predictions are being used to identify promising solvent-modifier system,<sup>2,3</sup> with other theoretical techniques<sup>4,5</sup> being used to generate the complex "phase diagram" from a limited number of solubility measurements, thus increasing the number of modifiers that can be investigated in a reasonable amount of time. In addition, we are evaluating the use of molecular modeling software (BioSym's Insight II operating on a Silicon Graphics workstation) for predicting solubilities. This is apparently the first application of molecular modeling techniques for prediction of SF solubilities. Preliminary results are promising: we have found a correlation between published experimental solubilities for model solutes and the energy change that is calculated when a solute molecule is inserted into a reasonably sized (e.g., 300-400 molecule) solvent matrix and the structure optimized as before to minimize energy.

1. J.M. Dobbs, J.M. Wong, R.J. Lahiere, and K.P. Johnston, "Modification of Supercritical Fluid Phase Behavior Using Polar Cosolvents," *Ind. Eng. Chem. Res.* 26, 56 (1987).
2. J.M. Dobbs and K.P. Johnston, "Selectivities in Pure and Mixed Supercritical Fluid Solvents," *Ind. Eng. Chem. Res.* 26, 1476 (1987).
3. A. Kramer and G. Thodos, "Adaptation of the Flory-Huggins Theory for Modeling Supercritical Solubilities of Solids," *Ind. Eng. Chem. Res.* 27, 1506(1988).
4. J.M. Wong, R.S. Pearlman and K.P. Johnson, "Supercritical Fluid Mixtures: Prediction of the Phase Behavior," *J. Phys. Chem.* 89, 2671 (1985).
5. S. Mitra and N.K. Wilson, "An Empirical Method to Predict Solubility in Supercritical Fluids," *J. Chromatographic Sci.*, 29, 305 (1991).

#### **Expected Payoff:**

Prevention of pollution associated with disposal of Army (and Navy) gun propellants; associated reduction of life-cycle cost of munitions.

#### **Milestones:**

FY93 (6.1): measure RDX solubilities in alternative (unmodified) SF solvents: develop molecular modeling techniques; use theoretical methods to predict solubilities for polar-modified CO<sub>2</sub> solvent systems.

FY94 (6.1): measure RDX solubilities for various modifiers/conditions; measure solubilities of binder components; correlate/interpret data with theoretical techniques. FY95 (6.2): measure LOVA binder, plasticizer solubilities; correlate/interpret data with theoretical techniques; design promising extraction/recycling schemes based on results.

FY96 (6.2): larger-scale experiments with full propellant formulations; explore & optimize propellant extraction/recycling schemes.

FY97-FY98 (6.3): Pilot-plant scale demo of most promising recycling scheme(s).

**Transition Plan:**

Progression is from 6.1 research into solubility relationships and modifiers (through FY94), then 6.2 research into extraction/recycling schemes beginning in FY95. If successful, technology transfer would take place via a pilot plant demonstration at a LOVA manufacturing site in FY97 or FY98; this would be a venture jointly funded by PM-TMAS and/or the Naval Ordnance Station, Indian Head, where LOVA gun propellant is currently manufactured.

**Funding: (\$K)**

FY93	FY94
400	450

**Performers:**

All research (6.1, 6.2) will be carried out in-house, but major interactions are expected with Battelle Northwest, University of Delaware, University of Wisconsin, and University of Texas (Austin).

This project will be closely coordinated with related projects at MICOM and RAAP (AP-based, and NC-based propellants, respectively).

**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Heavy Metal Discharge from Ship Ballast Tanks**

#### **Problem Statement:**

The U.S. Navy uses sacrificial anodes to provide corrosion protection of the seawater ballast tanks on ships and submarines. These sacrificial anodes are 99+ percent zinc metal and corrode to provide cathodic protection to the steel and non-ferrous components in the tanks. The amount of zinc discharged is not known but is potentially large. A typical ship may have between 5,000 and 25,000 kilograms (KG) of zinc anodes, which must be replaced at overhaul intervals.

The USEPA has recently suggested that wastewater containing a chronic concentration above 70 milligrams/liter (mg/L) total zinc be handled as a hazardous waste under RCRA Subtitle C. A limit of 700 mg/L total zinc would apply to acute concentrations. Operation of ballast tanks varies widely with engineering and operational requirements. The maximum corrosion rate of zinc in cathodic protection is well known, but the relationship to ballast tank water concentrations is not known. Discharge of ballast seawater which has a hazardous concentration of zinc is highly probable.

#### **Project Description:**

Several classes of ship ballasting requirements will be evaluated and compared to the zinc cathodic protection systems in use. Experimental determination of various zinc concentrations which can be achieved at different levels of cathodic protection. Standard electrochemical techniques will be used to determine the various rates of corrosion. This will be used in the development of a range of potential discharge concentrations.

Measurements of actual ship discharge should also be completed as a baseline comparison. Minor alternations to ballasting operations may limit discharge problems. Compilation of environmental conditions will provide additional information on the contributing factors. The effects of seawater temperature, salinity, pH, and dissolved oxygen will be investigated.

Alternatives to zinc sacrificial anode use will be evaluated. These include, but are not limited to:

- A. Aluminum sacrificial anodes
- B. Impressed Current Cathodic Protection using inert anodes
- C. Alternate corrosion control techniques

#### **Expected Payoff:**

All Navy and MSC ships have zinc anode cathodic protection in ballast tanks. Every port facility may be affected and environmental criteria for the discharge of zinc and zinc compounds is being tightened. This information will be applicable to the merchant fleet, power generating facilities, and the off-shore oil industries.



**Milestones:**

A. Electrochemical testing	FY93
B. Review of ballast tank criteria	FY93-94
C. Development of concentration data	FY94
D. Shipboard measurements	FY94-95
E. Alternative technologies	FY93-94-95
F. Recommendations for resolution	FY95

**Funding: (\$K)**

FY93	FY94
225	200

**Performers:**

NRL Key West, NRL Stennis, CD-NSWC Annapolis, and NAVSSES Phila.

**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Evaluating Clean Technology Implementation**

#### **Problem Statement:**

The goal of this project is to carry out 20 on-site assessments/evaluations of pollution prevention techniques and processes. The evaluations will be located at Army, Air Force, Navy, and Coast Guard bases, and other Federal facilities that have been participating in the EPA's Waste Reduction Evaluation at Federal Sites (WREAFS) program. Since 1988, the WREAFS program has supported 50 P2 assessments. In addition to identifying opportunities for waste reduction that were implemented, these assessments identified many opportunities to utilize new technologies that would lead to more pollution prevention. This SERDP project will support the implementation of new techniques and processes with evaluations of past and current assessments. Priority consideration will be given to DoD industrial operations that generate waste from plating, cleaning, and painting/depainting. It is a new program that will enhance the effectiveness of the existing WREAFS program.

#### **Project Description:**

The project is to carry out 20 on-site evaluations of reducing pollution prevention through implementing the recommendations of completed pollution prevention opportunity assessments (PPOA) for the EPA's WREAFS program. The 7 projects to be initiated in the first year are:

##### **Ozone Depleting Substance Alternatives:**

- 1) Evaluate alternatives for cleaning fuel control components within the wheel bearing overhaul process and eliminate the current CFC-113 vapor degreasing option using PD-680 or a hydrocarbon blend as well as aqueous and semi-aqueous cleaning alternatives.
- 2) Evaluate cleaning alternatives for electromechanical/electronic devices overhaul process by comparing baseline vapor degreaser/CFC-113 with final rinse alternatives of PD-680, Hydrocarbon blend, alcohol, and aqueous/semi-aqueous immersion cleaning process.

##### **Component Cleaning Alternatives:**

- 3) Evaluate methylene chloride cleaning alternatives within the engine exciter overhaul process to replace CFC-113 brush cleaning of exterior and interior parts with hydrocarbon solvents, such as ART 96, Axarel 6000, or Actvel 1160L.

##### **Naval Energy and Environmental Support Activity:**

- 4) Evaluate the implementation of 10 options for reducing coolant usage in machine shops.
- 5) Evaluate effectiveness of Aqueous cleaning in place of existing vapor degreasing activities and evaluate a closed-loop hard chromium plating process.

US Army Transportation Center:

6) Evaluate improved transfer efficiency systems for Chemical Agency Resistant Coating used to paint military field vehicles, and for recovery of thinners/solvents.

Joint Depot Maintenance Analysis Group:

7) TCE Substitute - Evaluate the effectiveness of an emulsion cleaner as a degreasing solvent and as an alkaline cleaner.

Many of these pollution prevention options are applicable to other DoD/DOE and private sector facilities where similar waste generating operations are being conducted. Since many of the activities require industrial products, it is important to include the private sector in the conduct of the evaluation. CRDA's will be developed for selected projects to enhance the usefulness of the outputs.

Technology transfer will result from project reports and project summaries from each of the tasks. These reports will be distributed through EPA, NTIS, and through a combination of active clearinghouses managed under PPIC. In addition, workshops and meetings will be conducted to assure technical quality of the tasks. A conference/workshop will be conducted at the end of each year to discuss the results of the project and discuss additional RD&D needs. This project will support the Federal Facilities Cooperative, which encourages temporary assignments for technical staff to work on these tasks with EPA technical staff.

#### **Expected Payoff:**

The tasks selected for this project will have wide applicability within DoD, DOE, and other Federal Agencies, such as NASA, USCG, DOI, because cleaning, stripping, painting, and plating relate to a myriad of manufacturing activities conducted in the United States and in other countries. The benefits to all users will be reduced wastes for a better environment. Added incentives will result in cost effective solutions to environmental problems, increased competitiveness in the market, with reduced waste, increased awareness, and enhanced image in the U.S. and internationally, and with reduced toxics, a safer environment for workers.

#### **Milestones:**

Ten project reports and project summaries	Year 1
Workshop/conference to discuss results of project	

Ten project reports and project summaries	Year 2
Workshop/conference to discuss results of project	

#### **Transition Plan:**

The Project will be coordinated with an initial meeting between the EPA Technical Task Manager (TTM) and the point of contact within the DoD. After the work plan has been prepared and jointly approved, an EPA support contractor will meet with both DoD and EPA contacts to begin the field evaluations. Each task will require close coordination by the

TTM at the site with, at least, 3 to 4 site visits over the life of the project. RREL will have an EPA support contract for each task. Meetings will be required to evaluate performance and make adjustments as necessary. The DoD may want to modify the targeted area during the initial meeting and adjustments will be made to ensure a useful evaluation.

**Funding: (\$K)**

FY93  
500

**Performers:**

The project will be managed cooperatively by the U.S. EPA's Risk Reduction Engineering Laboratory and the Department of Defense, Office of the Assistant Secretary for the Environment. Demonstrations are planned for Army, Air Force, and Navy Bases and the Joint Depot Maintenance Analysis Group. As part of this project two individuals from DoD will join the WREAFS program in Cincinnati for the duration of the project under an Interagency Agreement.

**Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

**Title:** Verification of Shelf Life Terms for Hazardous Materials

### **Problem Statement:**

Hazardous materials are often disposed of based on the expiration date on the materials container. There is a large body of anecdotal evidence that many of these materials may still be in usable condition. Unnecessary disposal of hazardous materials due to incorrect shelf life specifications results in both increased disposal costs and increased material replacement costs. As an example, a major Naval installation recently paid a disposal contractor \$320,000 to remove unopened containers of hazardous materials that had passed the shelf life dates printed on the container labels.

Work started on this effort in FY-91. Data were gathered on the 50 hazardous materials most often disposed of for reason of expired shelf life. Shelf life terms recommended by the manufacturer were compared to those used in similar, nonmilitary, applications. A number of important discrepancies were found and research into their validity was initiated. Work on this project in FY-92 was severely restricted by a low level of funding.

### **Project Description:**

The objective of this project is to verify the validity of manufacturers values of shelflife for products supplied to the DoD that contain hazardous materials. The technical approach has been to search the records of the DoD materials supply and waste disposal organizations to determine which classes or products (or specific products) are most often disposed of because of expired shelf life. Data on the dollar value of waste disposal and product replacement is also gathered. The shelflife terms of the products most often disposed of due to "expired" shelflife are then compared with the most similar commercial product. Where significant discrepancies exist, laboratory tests are performed to quantify the reason for the difference between DoD and commercial versions of the same material. Recommendations for changing the listed material shelflife are made and published.

### **Expected Payoff:**

Reduced hazardous materials purchases, inventory, and waste disposal costs will result. DoD-wide cost savings has not been estimated, but Naval Supply Systems Command (NAVSUP), NCEL's sponsor in this effort projected Navy savings in excess of \$50M annually. They have also endorsed our work, as expressed in the initial interim report, by assuring the Lab that this effort will be continued for a very long time. The emphasis, however, will shift to ship stores, since this is the source of a large fraction of the hazardous waste that develops from hazardous materials, simply because of a date on product labels.

### **Milestones:**

This ongoing project was closed down April 1992 with all other 6.3 environmental RDT&E projects at NCEL because of failure to receive FY92 SERDP funds in a timely manner. In continuation work, an interim report will be generated in FY93. This report will provide

recommendations for a second, larger group of hazardous wastes that will be selected by NAVSUP/NAVSEA for NCEL evaluation.

**Transition Plan:**

The results of the work done on this project will be presented directly to NAVSUP/NAVSEA for action. Revisions of shelf life terms and extensions can be expected, as will further tasking for laboratory work to study the storage behavior of specific hazardous wastes and their containers so that materials that have poor technical base information available can be scientifically assessed and realistic shelf life terms assigned.

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
200	150

**Performers:**

Navy/NAVFACENGCOM/NAVCIVENGRLAB with NAVSUP and NAVSEA. Active support from the National Association of Manufacturers (NAM) will again be forthcoming.

**Technical Points of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

**Title:** Advanced Nickel-Metal Hydride Battery (Adv Ni-MH<sub>x</sub> Battery)

### **Problem Statement:**

The goal of this program is to eliminate the use of cadmium metal, an EPA identified highly toxic substance, in rechargeable nickel-cadmium (Ni-Cd) batteries. The Air Force currently uses rechargeable Ni-Cd batteries for main aircraft batteries and other applications. After battery failure, disposal of cadmium containing cells is a costly and time consuming process. A new battery system, Nickel-Metal Hydride (Ni-MH<sub>x</sub>), completely eliminates the use of cadmium and has performance capabilities beyond that of Ni-Cd or lead-acid (Pb-acid) batteries.

### **Project Description:**

The objective of this program is to develop Ni-MH<sub>x</sub> batteries for use in a number of Air Force applications, thereby eliminating the need to handle and dispose of cadmium. The approach is to synthesize various metal-hydrides, fabricate cells (1-50 Ahrs) and test cells to characterize their performance (i.e., low temperature, cycle life, power output). Industry is exploring Ni-MH<sub>x</sub> technology to replace consumer Ni-Cd batteries. Initial results are very promising. However, this program is intended to elevate Ni-MH<sub>x</sub> technology to the high reliability and performance standards required for Air Force use. A major task within this program will be to investigate various MH<sub>x</sub> compounds and optimize cell performance for applications such as main aircraft, navigational and life support battery systems. The replacement of high maintenance, vented Ni-Cd main aircraft batteries with a 20 year Maintenance Free (Ni-Cd) Aircraft Battery (MFAB) is being addressed under an ongoing effort. The disposal of cadmium will be significantly reduced with the MFAB, but with the Ni-MH<sub>x</sub> it will be eliminated. The Advanced Ni-MH<sub>x</sub> program will provide batteries for flight test to prove the technology. Transition to users can follow a similar route established on the MFAB program.

### **Expected Payoff:**

Potential users of Ni-MH<sub>x</sub> batteries are widespread. Throughout DoD and the consumer market Ni-Cd batteries are used in applications from remote energy storage to powering radios. Furthermore, inherent to the Ni-MH<sub>x</sub> system is the elimination of maintenance. It is a sealed system which obviates the need to check or adjust electrolyte as is required for vented Ni-Cd or Pb-acid batteries. Elimination of flight line maintenance of vented Ni-Cd batteries is estimated to save the Air Force alone ~ \$1 billion over 20 years. Preliminary Ni-MH<sub>x</sub> data show that battery weight can be reduced to half of Ni-Cd or Pb-acid without sacrifice in performance. A detailed cost impact analysis for Ni-MH<sub>x</sub> has not been performed. However, based on studies conducted for replacement of Ni-Cd's with the MFAB, additional cost savings will be realized due to elimination of special handling and facilities needed to dispose of cadmium containing batteries.

**Milestones:**

This project is related to an ongoing effort, the MFAB, but takes a step further in complete elimination of the use of cadmium in rechargeable batteries. The first year of this effort will extend the requirements study of the MFAB which was primarily limited to main aircraft batteries. Cells will be fabricated and tested with known  $MH_x$  compounds and new  $MH_x$  formulations will be investigated early in the program. Battery development will occur the second year. Lessons learned from cell and battery development tasks will be incorporated into a final battery design and test article (deliverable) battery build for flight testing.

**Funding: (\$K)**

FY93	FY94
300	900

**Transition Plan:**

A transition plan exists to replace vented Ni-Cd's with the MFAB for ~ 100 operational B-52 aircraft. It is anticipated that Ni- $MH_x$  batteries will follow a similar plan to transition to other aircraft and other applications and/or be listed as a preferred replacement.

**Performers:**

Technical Monitors - USAF, Wright Laboratory, Aero Propulsion and Power Directorate, Battery Electrochemistry Section, (WL/POOS-2). Industry Involvement: Potential bidders currently conducting Ni- $MH_x$  development - Eagle-Picher, Hughes Aircraft, Ovonic, Gates - others.

Planned cooperative agreements: Potential DoD-wide cooperation through the Aviation Battery Standardization Group (AVBATS).

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Solvent Substitution and Low VOC Cleaners**

#### **Problem Statement:**

To identify low VOC (volatile organic compound) content cleaning solvents for use on Navy aircraft, weapon platforms, and ground support equipment (GSE), and to identify replacements for methylene chloride based chemical paint strippers. Volatile organic solvents such as methyl ethyl ketone (MEK) are used for solvent wipedown of aircraft prior to painting and post-painting cleanup. Other procedures require the use of stoddard solvent for cleaning aircraft parts in solvent tanks. Other degreasing and cleaning methods use high VOC cleaners. In addition, current chemical paint strippers contain hazardous components like phenols, methylene chloride and chromates and paint removal operations at maintenance depots has been determined to be a major contributor to hazardous waste generation in the DoD. Recently, OSHA has reduced the permissible exposure limit for methylene chloride from 400 ppm to 50 ppm, forcing users to make extensive changes in ventilation and personal protection. Regulations like the Clean Air and Water Acts, CERCLA, RCRA and local EPA and AQMD rules limit or prohibit the use and disposal of these hazardous materials. In addition, OPNAVINST and CNO directives require a 50-percent reduction in hazardous waste by 1992. Therefore, low VOC non-toxic alternatives to solvent cleaners need to be developed. In addition, there is a need to evaluate alternatives chemistries for paint removers for use at Naval Aviation Depots in order to identify a product or a chemistry capable of satisfying existing and future regulations while maintaining aircraft performance and operational readiness.

#### **Project Description:**

Solvent cleaners must be effective on a diverse combination of soils from baked-on carbon to aircraft greases and lubricants. This program will develop solvent blend formulations and aqueous cleaners which will be evaluated with laboratory performance and cleaning efficiency tests. The best materials will be further evaluated for vapor pressure, odor, evaporation rate, safety and cost. Enzyme cleaners, lubricant low VOC solvent cleaners, and supercritical CO<sub>2</sub> cleaning methods will also be evaluated in this program. Optimized materials will be service tested at a NADEP and transitioned to fleet use through specification modification and design changes. Non-methylene chloride alternatives must exhibit workable performance characteristics while reducing the impact of stripper waste on disposal operations. Because there are so many different substrates/alloys and coating systems currently used by the Navy, non-hazardous paint removers will also have to be versatile. This program will identify the best alternatives for ambient coating removal operations. Procedure efficiency, effects on substrate surface, hazardous waste generation and applicability will be investigated in order to determine the best procedure for Navy applications. The best alternative material will be demonstrated at a NADEP and transitioned to fleet use through specification modification and design changes.

### Expected Payoff:

The development of low VOC solvents would significantly reduce the total amount of hazardous materials emissions generated. In addition, the elimination of the methylene chloride based chemical paint strippers would significantly reduce the total amount of hazardous materials generated by Navy maintenance facilities. This effort is in direct support of Navy and DoD hazardous waste minimization policies/directives. In addition to reduced handling and waste disposal costs, Navy aircraft and equipment must be properly maintained. This is particularly important considering the cost of aircraft weapon systems and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also be transferred to many areas of the commercial sector (aerospace, automotive, marine, etc).

### Milestones:

	Status	FY
Evaluate low VOC solvents/processes	P	93
Evaluate/optimize stripper process parameters (Joint Navy/Air Force Program)	P	93
Initiate enzyme cleaner evaluation	P	94
Optimize low VOC solvents/processes	P	94
Service demonstration of optimized stripper materials (Joint Navy/Air Force Program)	P	94
Service demonstration of low VOC solvents/processes	P	95
Evaluate/optimize enzyme cleaners	P	95
Implementation of optimized stripper materials (Joint Navy/Air Force Program)	P	95
Implement optimized low VOC solvents/processes	P	96
Service demonstration of optimized enzyme cleaners	P	96
Initiate supercritical CO <sub>2</sub> cleaning investigation	P	96
Initiate lubricant low VOC solvent cleaners investigation	P	96
Implement optimized enzyme cleaners	P	97
Evaluate/Optimize supercritical CO <sub>2</sub> cleaning methods	P	97
Evaluate/Optimize lubricant low VOC solvent cleaners	P	97
Service demonstration of supercritical CO <sub>2</sub> cleaning	P	98
Service demo of lubricant low VOC solvent cleaners	P	98
Implement supercritical CO <sub>2</sub> cleaning	P	99
Implement lubricant low VOC solvent cleaners	P	99

P = Planned Milestone

**Transition Plan:**

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP and transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination throughout the development and evaluation of these materials/processes will ensure availability for implementation.

**Funding: (\$K)**

	FY93	FY94
Y817*	30	--
SERDP	170	120
TOTAL	200	120

\*Pollution Abatement (6.3B)

**Performers:**

Development of non-methylene chloride paint strippers is being performed by the Naval Air Warfare Center Aircraft Division Warminster (NAWCADWAR) and the Air Force (Tyndall AFB) in a joint effort. The solvent substitution and low VOC cleaner efforts are being performed by NAWCADWAR, Naval Aviation Depots and the Maintenance Technology Center for Environment and are being coordinated with efforts by the Air Force (Tinker AFB, Kelly AFB and Tyndall AFB), DOE and aerospace industry (MCAIR, Boeing, etc.).

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Non-Emulsifying Degreasers for Shipboard Use**

#### **Problem Statement:**

Most Navy ships are equipped with on-board oil separators for de-oiling bilge water prior to overboard release at sea or transfer in port to "Doughnuts," which are floating oil-water separators that release the water phase to the harbor at the same rate as bilgewater is introduced into it. Use of degreasing compounds aboard ship can cause serious problems with this procedure, since some degreasers form very slow breaking water/oil emulsions that are unsatisfactorily separated by the shipboard oil/water separator, the Doughnuts, and even shore-side water/oil separators that are considerably more sophisticated than the first two configurations. As a result, bilgewater in some ships is received with unacceptable oil levels, Doughnuts produce oily films on the harbor water, and large quantities of interphase emulsion is collected from shoreside DAF units and this material must be stored for very long periods of time to wait out separation. Use of persistent-emulsion forming degreasers must be discontinued and this can only be accomplished by identifying degreasers that will form fast-breaking emulsions while fulfilling the various functional criteria. NCEL has initiated a project for achieving this goal. Rational criteria have been established for qualifying degreasers as functionally acceptable and fastbreaking. The goal now remains to apply these criteria to a wider battery of candidate degreasers (34 have already been tested; only 4 qualified) and then introduce into the fleet for field evaluations the products that are found qualified.

#### **Project Description:**

The NCEL degreaser criteria and testing protocol will be applied to a large population of candidate materials. In the preceding test work, the sampling was arbitrary or random since the main objective was to validate the criteria and demonstrate the reproducibility and correlatability of the test methodology with the parametric performance of the materials tested. In the present resumption of this work, the technical objective will be to exercise the methodology with a maximum number of candidate materials so that serviceable materials can be identified that have both met laboratory criteria and shown equally acceptable performance under rigorous field use. This experience will permit the development of more effective degreaser specifications, allow the testing procedures to be refined, establishment of optimum degreaser performance criteria, and, incidentally, furnish a family of materials that will be acceptable for shipboard cleaning applications. The technical risks associated with this phase of work are minimal, given the success that has been achieved in the preceding work. This work will be done with the support of NAVSEA Code 5, which has strongly endorsed the work.

#### **Expected Payoff:**

Handling of bilge and ballast waters will be greatly simplified when persistent emulsifiers are eliminated from use in the fleet. Shipboard oil/water separators will be able to function properly, shore-side bilge water treatment plants will have to contend with a much smaller volume of oily water. The aqueous phases will be consistently acceptable for NPDES

discharge and the oil phase for cofiring or DRMO sale. The avoidance of NOV's and resulting fines, coupled with downturn of bilge water treatment requirements and prolonged storage of emulsified liquid, will result in cost savings in the tens of millions of dollars.

#### **Milestones:**

Conduct qualification testing, and upgrade methodology and criteria;	FY93
Perform field testing in fleet, validate laboratory correlation;	FY94
Prepare documentation (RDT&E report, specifications, buyers list);	FY94

#### **Transition Plan:**

Industry will provide the products that will be qualified or rejected. Reformulations and new formulations may be submitted, if done in a timely manner. Coordination between User and NCEL will be indispensable and from previous liaison with CINCPACFLT will be enthusiastic and effective. All Navy Yards have been requested to participate and all have indicated an early readiness to furnish available bottoms for field testing of NCEL-qualified degreasers. Upon completion of the project work, a test results report, sample specification, and materials list will be turned over to the appropriate Item Manager at NAVSUP for implementation of product use.

#### **Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
190	175

#### **Performers:**

Navy/NAVSEA/NCEL in joint effort with CINCPACFLT and, possibly, CINCLANTFLT

#### **Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

### **Title: Minimization of Solvents used in Analyzing Mixed or Hazardous Wastes**

#### **Problem Statement:**

In recent years, the New Brunswick Laboratory (NBL) has identified the need to independently reduce its volume of waste, specifically mixed waste. More time and funds must be devoted to waste minimization efforts. To accomplish waste minimization at NBL, several potential projects have been identified which involve the modification of analytical methods used at NBL and throughout the DOE complex. The goal of the modifications will be to substitute RCRA-regulated reagents with non-RCRA-regulated reagents used in analytical procedures. For these projects to be realized, more time and funds must be committed.

**Waste Streams Generated:** Waste generated from analytical procedures performed at NBL is treated, stored and disposed through ANL-E Environment and Waste Management Program (EWM). NBL's waste streams can be categorized into hazardous, radioactive (including uranium and transuranics (TRU)), and mixed (hazardous and radioactive). NBL is one of the largest generators of liquid mixed and solid radioactive combustible/compactable waste on the ANL-E site. This project is new and has not been previously funded.

#### **Project Description:**

Waste minimization was not the primary goal in the development and use of analytical procedures in the past. Waste was generally collected by ANL-E EWM, and the method of treat, store and dispose (T/S/D) was not an issue until recently.

NBL has taken some preliminary steps to incorporate waste minimization in laboratory procedures. Where possible, NBL stopped using analytical methods which generated mixed waste such as amperometric titration of plutonium. The procedure used RCRA-listed chemicals such as arsenic, mercury, and dichromate. For all analytical procedures, the quantities of reagents are kept to a minimum, which in turn minimizes the volume of waste. Also, NBL has started separating and neutralizing titration blanks (hazardous waste) from titration products (mixed waste) to minimize the volume of mixed waste generated at NBL.

The primary objective of NBL's waste minimization projects would be the modification of safeguards analytical procedures which are used by NBL and DOE-contractor facilities.

The following points would need to be considered when analyzing each procedure:

- a) Determine the classification and the quantity of waste generated by the method.
- b) Evaluate the feasibility of scaling down the reactants.
- c) Consider using alternate reagents which are not RCRA-listed.
- d) Consider developing alternate methods which use smaller sample size.
- e) Maintain the precision and accuracy needed for accountability of nuclear materials.

Once a procedure has been identified as a candidate for waste minimization, the method can

be selected for evaluation. The following tasks need to be completed before a procedure can be routinely used by NBL and the technology transferred to other laboratories:

- a) Testing and documentation for the revised method.
- b) Statistical evaluation for establishment of precision and bias statements for the method.
- c) Documentation of the procedures in the NBL manual.

The basis for proposing these projects are to search and establish environmentally sound/safe/sensible analytical methods for the nuclear material safeguards program.

#### Tasks and Activities:

##### A) Review Analytical Procedures

NBL plans to review as many active procedures as possible. NBL has 58 active procedures in its Procedures Manual. Development of new methods is ongoing. The driver was to keep up with the latest measurement technology and to improve precision of already existing methods by incorporating newer technological advancement into the analysis steps. Waste minimization was not previously the driver for the analytical method development at the laboratory.

##### B) Modify Davies and Gray Uranium Titration

This method is used to determine the uranium content of samples from virtually every point in the nuclear fuel cycle. The Davies and Gray method (1) as first described in 1964. The procedure was further improved and thoroughly evaluated at NBL. NBL reported first the application of this titration to the analysis of a large variety of uranium alloys, uranium metal, and uranium compounds (2). NBL also reported improving the precision and accuracy of the method (3,4). The precision and accuracy of the NBL basic procedure are well within 0.1%. This procedure, referred to as the NBL-modified Davies and Gray method, is used in the nuclear industry nationally and internationally.

The action plan would include trials of chemical oxidants and free electrons. Two independent experiments will be conducted. In one experiment, ceric sulfate will be tested as the chemical oxidant to replace the dichromate. In the other experiment, the reaction mixture will be titrated using electro-generated Vanadium (V). This method, uranium coulometry, would involve setting up the coulometry cell-electrode system and the electronics necessary to measure coulombs. The performance of the methods have to be statistically evaluated, and the procedures require formal documentation prior to their use in accountability measurements.

##### C) Uranium Ion Exchange for Sample Preparation

The NBL-modified Davies and Gray titrimetric method is versatile in the sense that uranium samples can be directly assayed yielding accurate and precise results without any prior purification of the sample. Alternate methods to the NBL titrimetric methods (i.e., uranium coulometry) cannot be used directly and will require a purification step prior to sample analysis. Ion exchange columns that are commercially available will be used to test a variety

of uranium samples that are analyzed at the laboratory. The testing would involve determining to what extent the ion exchange can clean and separate uranium from other impurities.

#### D) Uranium Isotope Dilution Mass Spectrometry

This method involves assay of uranium by mass spectrometry using the isotopic dilution technique. In the isotope dilution methods, a known amount of a tracer isotope of the element to be determined is added to a known amount of sample, the element is separated after steps have been taken to insure that the tracer and sample constituent are in the same chemical form, and an isotopic analysis performed. The observed isotopic dilution of the tracer is used to calculate the original concentration of the element in the sample. For uranium assay, U-235 or U-233 tracer will be used. With the availability and advancement of mass spectrometers, this method has greater applicability now than in the past. This technique was selected because the analysis requires very small sample size thereby reducing the amount of waste generated in the process.

#### Expected Payoff:

An NBL-specific waste minimization program will allow NBL to further reduce its waste volume. If NBL takes an aggressive role in minimizing its own waste at the generation point, ANL-E EWM Program will also benefit.

The benefits of this project are not limited to NBL, but extend to all the DOE-contractor laboratory facilities that have analytical methods for accountability measurements. Many laboratories participate in the NBL inter-laboratory Safeguards Measurement Evaluation Program. NBL will keep these labs informed about the methods that will be tested and possibly adopted in the future. MBL will assist these labs in establishing the newer or modified methods at their facilities.

The importance of the MBL-modified Davies and Gray method and the frequency of use of this method in the DOE complex has made it a top candidate for waste minimization. NBL has the expertise in this method. It is a major advantage to the DOE community for NBL to take the lead role in establishing modified procedures for uranium accountability measurements which also minimize waste production in DOE.

#### Milestones:

Title: Review Analytical Procedures

1. Chemist/Physical Scientist review active procedures.
2. Collect information about other applicable methods.
3. Enter information into a spread sheet.
4. Analyze the spread sheet and group the methods.
5. Select methods that should be studied.
6. Prepare project plans for these methods.



Title: Modify Davies and Gray Uranium Titration (Cerium titrant)

1. Obtain Cerium compound and investigate impurities.
2. Perform preliminary titrations.
3. Write draft procedure.
4. Assay pure materials.
5. Statistical evaluation.
6. Test method on regular samples.
7. Purify regular samples and test the method.
8. Final procedure.

Title: Modify Davies and Gray Uranium Titration (Coulometry)

1. Setup coulometry system.
2. Test system and perform preliminary titrations.
3. Evaluate system accuracy/precision for the method.
4. Write draft procedure.
5. Purify regular samples and test the method.
6. Final procedure.

Title: Uranium Ion Exchange for Sample Preparation

1. Obtain all different uranium samples analyzed previously.
2. Prepare samples using ion exchange columns.
3. Analyze samples using x-ray, gamma, Mass Spec, and titration.
4. Analyze all results for the different samples.
5. Write procedure.

Title: Uranium Isotope Dilution Mass Spectrometry

1. Use samples purified by ion-exchange for analysis.
2. Obtain uranium spike and reevaluate the material.
3. Statistical plan and preparation of sample-spike.
4. Analyze samples.
5. Statistically evaluate the data.
6. Final Procedure.

#### **Transition Plan:**

The milestones include implementation of the methods at NBL. The transfer of the methods to DOE-contractor facilities can be accomplished through the NBL Safeguards Assistance and Safeguards Measurement Evaluation programs.

**Funding: (\$K)**

FY93	FY94
360	360

**Performers:**

DOE-NBL will be the lead performer with constant input and recommendations from DOE-contractor analytical laboratory personnel.

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## **SERDP Thrust Area: Pollution Prevention**

**Title:** Expanding the Pollution Prevention Information Exchange System (PIES) to Serve as a Communication and P2 Network of Technical Information for Other Federal Agencies

### **Problem Statement:**

The goal of this project is to expand the PIES computer network to serve the P2 networking needs of other federal agencies. The expanded network would centralize: case study and process modification information; solvent alternative options; alternatives to Ozone Depleting Substances; experts; and ongoing research. The system would present existing data base tools from each Agency (i.e. PIES case study data base; INEL Solvent Substitute Handbook data base; DoD NMERI halocarbon data base). The agencies would pool technical knowledge and experience on case studies, process/raw materials substitutes and research projects. Each agency will assist in adding technical P2 information to the network through individual efforts, contract acquisition requirements, contract P2. Information recording requirements, office initiatives, etc. PIES will be linked to and used in conjunction with other P2 information services within each agency such as the Navy Halon and CFC Clearinghouse, and the Air Force ProAct Hotline. The agencies would all participate in a federal materials exchange service which would make wastes, spent products, and excess inventory, available for raw materials use through the PIES network. The project would include the establishment of "satellite nodes" of the PIES network within each agency to allow an Internal P2 communication network to be established which would link to the national and international portions of the PIES network.

The project targets each service and base of DoD; over 180 DoE facilities including all national laboratories; DOI (Bureau of mines); and GSA. The USAF/Pollution Prevention Division of the Center for Environmental Excellence and the Army Acquisition Prevention Supply Office will take the lead for DoD while the Office of Energy Research and the Office of Environmental Restoration and Waste Management will take the lead for the DOE portion of the project.

EPA established PIES in 1990 as the computerized component of the Pollution Prevention Information Clearinghouse (PPIC). PPIC was created to assist in networking technical and programmatic information to all levels of government, industry, academia, and international organizations. EPA was required under the Pollution Prevention Act of 1990, to formally establish a national clearinghouse. PPIC and PIES assist in fostering the establishment and growth of P2 programs in government and industry. PIES creates a forum for exchange of experience and information with experts in the field.

PIES is an electronic bulletin board system that has been integrated with over a dozen software packages to relay a network of P2 related data base tools. PIES is an interactive P2 network where users communicate through a series of message centers and can up and down load information files. The PIES network has been integrated with the SprintNet packet switching network (yielding access to 99 other Packet Switching Networks (PSNs)), the EPA X.26 network, the Internet, 800 toll free lines and toll telephone lines creating a variety of access routes. The network is fully expandable and currently supports 39 simultaneous users. PIES presently supports approximately 5000 users, has an average of 125 new users per

month, and averages 70 incoming calls per day. The present PIES configuration relays 3 separate networks and more than 12 data base tools. The network includes PIES, the International Cleaner Production Information Clearinghouse (ICPIC), and the Ozone Action Information Clearinghouse (OAIC) (the latter two being joint efforts with the United National Environment Program (UNEP)). Data bases include literature search functions for case studies, general publications, state and federal program descriptions, contracts, grants, research, enforcement, and OZONET - a series of solvent substitute data bases.

The basic concept behind PIES as an interactive network is to become a national resource of P2 information maintained by its users. Centralized knowledge bases and communication with peers can provide an immense resource by enhancing communication, avoiding duplication of effort in research and promoting joint efforts which pool experience and resources.

Both DoD and DoE have expressed interest in using PIES to establish a P2 computer network in each of these agencies. Expansion and upgrade of PIES for DoD and DoE use is consistent with priorities within each agency to promote and adopt pollution prevention programs resulting in stringent proposed reductions in overall waste generation volumes by 1995 and 2000. Both agencies have expressed a need for typical PIES information such as case studies, and do not want to create redundant separate information networks. Conducting research to improve the PIES network to a relational, intelligent network capable of connecting with high speed transmission networks is consistent with the high performance computing initiative of DOE.

PIES presently represents an expanded BBS network with state of the art connectivity to packet switching and other communication networks. Although PIES provides an array of data base tools the network is not operated in a relational or window capable environment. This research project would determine and create an appropriate operating platform to allow PIES users to operate in a "point and click" environment allowing all data base tools to be accessed simultaneously. Research is necessary to determine how PIES can be upgraded to allow incorporated of an intelligent front end to access reprogrammed relational data base tools in a windowed environment. Research also needs to be conducted to enable the connection of this network to DoD's Autovon (data switch) network, and DOE's Energy Sciences Network (ES net). Additional steps of this project would include the incorporation/addition of data bases/clearinghouses currently funded by DoD and DoE such as the INEL Solvent Handbook; the NMERI Halocarbon Alternative Testing Data bases; and the Navy halon and CFC Clearinghouse to create centralized national knowledge bases. DoE will also use the PIES expansion research as a pilot test for a more expansive DoE communication network covering more than P2 issues.

PIES data content will also be enhanced through this project especially in the areas of mixed low level radioactive wastes and associated alternatives; and halon/CFC, and solvent alternatives as well as halon and CFC banking alternatives under the PIES Ozone Action portion of the network as relayed through EPA's Significant New Alternatives Program and through the interim Multilateral Ozone Fund under the Montreal Protocol.

Other new data base tools will also be created by DoD, DoE, DOI, and GSA for inclusion in the PIES network, such as a federal Agency Surplus Inventory Exchange. This type of

networking tool would further reduce the volume of wastes disposed by federal agencies by reusing alternate materials as raw materials in various processes.

### **Project Description:**

Conduct research, pilot test, and implement an expanded PIES network by establishing DoD and DOE PIES satellite nodes. The research and implementation tasks are designed to establish PIES as the state of the art in electronic information transfer. Objective would include the linkage of these PIES satellites to high speed transmission networks; establish relational data manipulation and windowing capabilities throughout all PIES data base tools; create national knowledge bases and umbrella networks for federal P2 information such as solvent use alternatives; and create new networking data bases to be presented through the PIES framework, such as a Federal Agency Surplus Inventory Exchange.

Using a working group comprised of DoD, DoE and EPA representatives, alternate PIES BBS platforms will be evaluated by considering current and future agency needs and capabilities. DOS vs UNIX environments will comprise the initial comparative evaluation. Once a platform has been agreed to, EPA and DOE will lead experimentation and pilot testing of the DOE satellite nodes and necessary high speed transmission linkages to a dedicated high speed transmission line such as a 56K T1 line. A similar pilot will be conducted with DoD and its Autovon network. EPA will lead an effort to merge DoD, DoE and EPA data base tools with the direction of the working group. DOI, GSA, and DOE will comprise a subgroup to identify needs for a surplus inventory exchange. EPA will construct this surplus materials network using programming previously designed for a national waste exchange network.

#### **Tasks:**

- 1) Establish working group
- 2) Establish DoD/Service miniexchange on PIES
- 3) Conduct PIES operating platform evaluation
- 4) Establish new or modify existing PIES platform
- 5) Establish DOE satellite node
- 6) Pilot test DOE ES net connectivity
- 7) Conduct DOE outreach and training
- 8) Establish DoD satellite node
- 9) Pilot test DoD Autovon connectivity
- 10) Conduct DoD outreach and training
- 11) Convert all PIES data bases into relational data bases with intelligent front and access mechanism.
- 12) Research, test and implement windowing and ASCII transmission functions
- 13) Test transmission of windowed information through DoD and DoE satellites
- 14) Identify and modify DoD and DoE data bases to be included under the PIES umbrella
- 15) Collect information and conduct final programming of federal agency surplus inventory data base and implement on PIES
- 16) Conduct intra agency follow-up to determine efficiency of modified PIES network with individual DoD and DoE users
- 17) Maintain workgroups to continuously assess user feedback, and to collect information

This project is consistent with the primary objective of both Agencies to reduce waste

generation by implementing pollution programs, options, and techniques. Both agencies have committed to Congress to serious reductions in waste generation. The PIES network is designed to foster this concept through the transmission of state of the art programmatic and technical P2 information. Designing an information network that is on the edge of information management concepts is consistent with DOE's high performance computing initiative.

EPA has funded the development of the PIES network since 1988. This project is consistent with EPA's goals for this network and its own pollution prevention initiative. DoD has been pursuing a proposed MOU with EPA, known as Toxics Reduction in the Military (TRIM) to establish a number of pollution prevention joint projects, one of which was to be the expansion of the PIES network.

#### **Expected Payoffs:**

Foster the growth of P2 programs and adoption of P2 technology at all DoD and DoE facilities assisting these agencies in meeting their national commitments, by reducing the generation and disposal of wastes.

Combine DOE and DoD P2 technology and case study information into national knowledge bases for the benefit of all government, industry, and academic users of the PIES network.

Broaden information resources accessible to PIES users by adding DoD and DoE data base tools to the network.

Assist DoD and DoE facilities in meeting the CFC bans under the CAA and the Montreal Protocol through option conveyed in the OzonAction portion of the PIES network.

Meet DoE's high performance computing initiative by enhancing the speed, capacity, and graphic windowing capabilities of PIES through connection to ES net.

Enhance global connectivity to PIES to academic, international, and governmental users by improving Internet access through Es net.

Allow easier use and access to PIES technical information through intelligent access to relational formats.

Expand the national resource of P2 information; as well as the forum for P2 research and expertise.

#### **Milestones:**

2/93-8/93:

Convert all PIES data bases into relational data base with intelligent front end access mechanism; Identify and modify DoD data bases to be included under the PIES umbrella; Collect information and conduct final programming of federal agency surplus inventory data base and implement on PIES; Establish USAF and Army miniexchange as test beds for

information collection; Establish working group; Complete PIES operating platform evaluation; Establish new or modify PIES platform; Research, test and implement windowing and ASCI transmission functions.

9/93-12/93: Establish DOE satellite node; Test transmission of widowed information through DoE satellite; Pilot test DoE net connectivity; Initiate DoE outreach and training.

2/94-10/94: Pilot test DoD Autovon connectivity; Initiate Intra-agency follow-up to determine efficacy of modified PIES network; Establish DoD satellite nodes; Initiate DoD outreach and training.

#### **Transition Plan:**

Interagency working group will initiate and direct scheduled activities. EPA will report back to the working group as each phase is completed. training module will be conducted on a regional basis for each agency once each satellite has been implemented. Follow-up analyses will be conducted with individual laboratories and bases to determine effectiveness of the network and usefulness of information conveyed. Where possible data gaps will be identified for future research.

#### **Funding: (\$K)**

	<b>FY93</b>	<b>FY94</b>
SERDP	900	
EPA	100	200
DOE	**	**
DoD	**	**

\*\*Doe and DoD will provide funding input on approval of budget if SERDP is awarded (funding range estimated between 50 to 200K)

#### **Performers:**

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#### **Technical Point of Contact:**

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## **SERDP Thrust Area: Pollution Prevention**

**Title:** Contribution of Mixing to Formation of NO<sub>x</sub> in Gas Turbine Combustors

### **Problem Statement:**

The goal is to quantitatively characterize the effect of mixing efficiency in interrogable glass wall-jet combustors on the quantity and distribution of NO<sub>x</sub> formed during combustion of synthetic fuel mixtures, and use the data so obtained to generate a predictive computational model for NO<sub>x</sub> formation. WL/POSF is the targeted organization.

NO<sub>x</sub>, which forms as a byproduct of imperfect combustion, is a regulated emission from fixed sources. Pending regulatory action is expected to extend regulation to jet engines during testing and in operation. Current trends in engine design appear to portend hotter, faster combustion, which will aggravate the problem of NO<sub>x</sub> emissions unless significant improvements are made to combustion technology. If successful, the results of this effort will contribute to design improvements that will improve the compliance status of the next generation of jet engines.

This is a new SERDP program. It supports AFWAL/PO--AFESC/RD Memorandum of Understanding, "Environmental Quality Research and Development in Support of the USAF Aero Propulsion Fuels Research and Development Program," dated 21 June 89.

### **Project Description:**

The technical objective is to quantify mixing characteristics and local concentrations of NO<sub>x</sub> under precisely defined conditions of combustion and to extract a predictive, quantitative, computational description of the relationship of NO<sub>x</sub> concentration to controllable mixing parameters.

The technical Approach is to apply high-speed optical methods of interrogation to determine maps of local concentrations of key species, temperature, and rates of motion and relative motion within the reactive fluid in glass-wall jet combustors. Develop and revise evolutionary models to describe the experimentally-determined behavior, by making and testing predictions.

Tasks associated with the project include 1) Surmise a reasonable mechanism for NO and NO<sub>2</sub> production and removal; 2) Measure formation and removal rate constants for NO and NO<sub>2</sub> in the test combustor; 3) Develop an interpretive computational model; 4) Design and execute tests of the predictive capability of the model; and 5) Refine the model to provide best possible fit to full data set.

This project fits in section 2.B.2 of tri-service strategic plan, parallel to Formation and Control of NO<sub>x</sub>. Earlier efforts from this lab examined formation and control of soot and transitioned to control of NO<sub>x</sub> emissions from jet engine test cells. WL/PO is involved in new engine design, and will assume the results of this program as a component of the armamentarium of design tools.



Risks are moderate - the extent to which enhancement and control of mixing can decrease NOx concentrations exiting a jet engine might be minimal.

**Expected Payoff:**

AF (and other DoD and civilian agencies) will be better able to comply with regulatory standards for emission of NOx from jet engines as mobile sources under Title 2 of the Clean Air Act Amendments, or to comply without compromising standards of performance.

**Milestones:**

Modification of lab facilities	0-3 months
Shakedown testing	2-4 months
Mapping temperature and flow fields	4-12 months
Mapping of concentrations of NO & NO <sub>2</sub>	12-18 months
Initial model of NO & NO <sub>2</sub> formation and removal	16-18 months
Refinement of model by prediction and experimental validation	18-35 months
Final report	36 months

**Transition Plan:**

Data and the computational model will be delivered to WL/PO and distributed among the commercial engine manufacturers for incorporation into their respective design codes.

**Funding: (\$K)**

<b>FY93</b>	<b>FY94</b>
240	240

**Performers:**

The performer will be Combustion Laboratory, Department of Mechanical Engineering, University of California, Irvine. The project is not suitable for a CRADA.

**Technical Point of Contact:**

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## **MODIFICATIONS/GUIDANCE TO PROPOSALS AS RECOMMENDED BY THE SERDP SCIENTIFIC ADVISORY BOARD**

The Scientific Advisory Board convened three meetings in the conduct of reviewing FY 1993 proposals. The comments below reflect specific guidance and/or modification provided to the proposer during the course of recommending approval for funding. Thus, the guidance provided is not inherently noted within the project descriptions found within other sections of this document.

### **"Assessment and Management of Risks to Biodiversity and Habitat" (Conservation)**

The SAB recommended approval for providing 1 million of SERDP FY93 funds to the program but recommended that the funds be limited to support the West Coast Transect Project. Specially, the Board recommends modifying the major deliverables of the proposal to focus on DoD concerns (military risk assessment, T&E species on military bases). Furthermore, the Board recommends continuation of the three year effort dependent on a successful review of the modified proposal and an annual review of successful attainment of milestones.

### **"In-Situ Treatment of JP-5 Unsaturated Soils" (Installation Restoration)**

The Board recommended approval for funding, however they requested that the task to develop a DNA-based detection system for microorganisms that degrade JP-5, to be separately funded by the Air Force, be directly linked to the project's milestones and measures of success.

### **"Field Research at Wurtsmith AFB" (Installation Restoration)**

The Board recognized this proposal as a unique opportunity to coalesce the research advancements in biotechnology. The proposal was recommended for approval with the assurance that this would not necessarily be the only national bioremediation site.

### **"Ecotox Data Base" (Installation Restoration)**

The Board expressed concern that the proposal's objectives should be accomplished by EPA. However, they did agree that this effort is needed and funds be provided for only one year to initiate the effort. This recommendation includes their desire to send a clear message to EPA that follow-on data entry and data base maintenance should become a multi-agency responsibility and cost-sharing program in the outyears.

"Toxicology and Human Health Risks" (Installation Restoration)

The Board was in agreement on the need and importance of this research, and suggested that the Principle Investigator turn some of the attention to identifying exposure pathways. Fate and transport modeling would, according to the Board, give more meaning when quantifying the effects of TCE in human tissue. The Board also suggested that the proponents solicit the expertise of Dr. Roger McClelland of the Chemical Industry Institute of Technology. The proposal was unanimously recommended for FY 93 funding.

"Non-hazardous, Low VOC Corrosion Protection Paints and Coatings" (Pollution Prevention)

After considerable discussion regarding the lack of support from the U.S. chemical industry in their quest to develop environmentally compliant paints and coatings, the SAB recommended approval for funding one year of this effort. This approval is contingent with the understanding that it is the Navy's responsibility to provide outyear funding from its Tech Base and Advanced Technology Development programs.

"Alternatives to Halon 1301 for Ground Vehicle Crew Compartments" (Pollution Prevention)

The Board appreciated the magnitude and significance of the proposals objectives but could not justify \$20 million over the next few years for a unique, limited Army/Marine issue. The SAB recommended approval for funding one year of this effort with the understanding that it is the Army's responsibility to fund the outyear requirements; joint funding options will be considered.

"Plutonium and Uranium Metal Forming Technologies" (Pollution Prevention)

Dr. Parker was asked by the Board at the previous meeting to provide a technical assessment of the efficacy of this technology development in light of the fact that weapons production had markedly decreased. While it was clear that a 50% reduction in production waste is a major accomplishment, the overall costs of the project remain a concern. However the project was one that provided identifiable accomplishments during the previous funding period. The Board recommended approval of FY93 funding, but will be reluctant to provide any follow on funding due to the questionable cost/benefit ratio at this juncture.

"Supercritical Water Oxidation Technology Demonstration" (Compliance)

An initial rejection by the Board was rescinded after a reclamation was submitted by the Navy and the Office of the Deputy Undersecretary of Defense (Environmental Security). Dr. Weber was asked to provide a thorough technical assessment of this revised proposal and he agreed that Phase I warranted receipt of FY93 funding. However, he underscored a need to review the program and followon plans prior to receipt of continued funding.

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